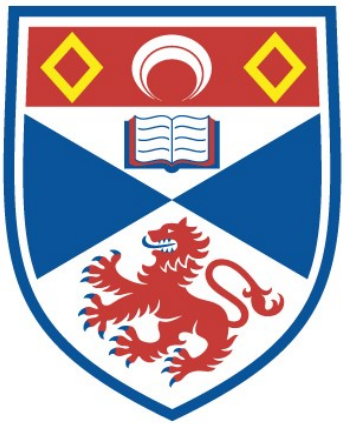
MODIFICATION OF POLYDIENES VIA HOMOGENEOUS CATALYSIS

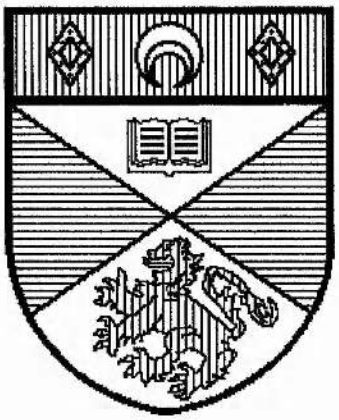
Mairi Nicol

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1998

Modification of Polydienes via Homogeneous Catalysis



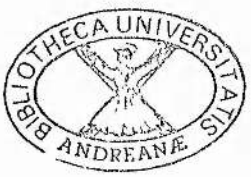
a thesis presented by

Mairi Nicol

to the

University of St Andrews

in application for
The degree of Doctor of Philosophy



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To my mum and dad
and my brother and sister; Anne and Mark
and my two year old neice Alison
for all their help and support.

DECLARATIONS

I, Mairi Nicol, hereby certify that this thesis, which is approximately 40,000 words in length, has been written by me, that it is the record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

Signed Date

I was admitted as a research student in October 1993 and as a candidate for the degree of Ph. D in October 1994; the higher study for which this record was carried out in the University of St Andrews between 1993 and 1996.

Signed Date

I hereby certify that the candidate has fulfilled the conditions of the resolution and regulations appropriate for the degree of Ph. D in the University of St Andrews and that the candidate is qualified to submit this thesis in application for that degree.

Signature of Supervisor Date

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The Perfectionist

Her organisational skills are second to none
One can be sure her will be done
There's never any need to fear
There's never any mishaps here

She's a stickler for neatness and cleanliness too
A haphazard fashion will never do
Everything has to be just so
Nearly clean would never go

Her every fibre oozes creativity
It's here we realise her naiveté
For simple attitudes nurture beauty and wonder
For us perhaps a moment to ponder

Her faults it appears (at first) she hasn't any
But like everyone else she has a few - not many
She strives to be in tune with her perfect environment
She'll still be trying when she reaches retirement

Her moods are sombre like the thundery sky
No one would say this was a lie
But she comes smiling through in her usual way
And tries again to perfect another day.

Theresa Nicol (1996)

CONTENTS

CHAPTER 2

EPOXIDATION

CHAPTER 3

ISOMERISATION

CHAPTER 4

OXIDATION

CHAPTER 5

FUTURE WORK

CHAPTER 6

EXPERIMENTAL

ABBREVIATIONS

AAS..... Atomic Absorption Spectrometer

acac..... Diacetylacetone

AD-mix..... Asymmetric Dihydroxylation-mix

amu..... Atomic mass unit

Ar-BIAN... Bis(arylimino)acenaphthene

BBN..... Boranbicyclononane

Bu^tOH..... Tertiary butanol

Bu^tOOH.... Tertiary butylhydro peroxide

CAT..... Catalyst

CH_2Cl_2..... Dichloromethane

CHN..... Carbon, Hydrogen and Nitrogen

cm^3..... Cubic centimetres

C=O..... Carbonyl

DHQ..... Dihydroquinine

DIPPP.....1,3-bis-(diisopropylphosphino) propane

DME..... 1,2-dimethoxyethane

DMF..... Dimethyl formamide

DMI..... Dimethyl imidazolidinone

DMPU..... Dimethylpropeneurea

DMSO..... Dimethyl sulfoxide

DPPB..... 1,3-bis(diphenylphosphino) butane

DPPE.....1,3-bis(diphenylphosphino) ethane

DPPP.....1,3-bis(diphenylphosphino) propane

DSC..... Differential Scanning Calorimetry

DTA..... Differential Thermal Analysis

ECO..... Ethene-carbon monoxide

FTIR..... Fourier Transform Infrared

HCl..... Hydrochloric

HFIPA..... Hexafluoro isopropyl alcohol

HMPA..... Hexamethylphosphoramide

HMWT..... High molecular weight

HPLC..... High Performance Liquid Chromatography

KOH..... Potassium hydroxide

LiBr..... Lithium bromide

n-BuLi ..... n-Butyl lithium

LMWT..... Low molecular weight

μgcm^{-3}.....Micrograms per cubiccentimetre

mmol..... Millimoles

Mn..... Number average

Mol..... Molecular

$Moldm^{-3}$..... Moles per cubicdecimetre

$[MoO_2Cl_2L]$.... Dichloro(diethoxy phosphorylcamphor) dioxomolybdenum (VI)

MPT..... Melting point

M.W..... Molecular weight

NaCl..... Sodium chloride

NaH..... Sodium hydride

NaI..... Sodium iodide

NaOH..... Sodium hydroxide

NM..... Nanometres

NMR..... Nuclear Magnetic Resonance

OBS..... Observed

^oC..... Dergees centigrade

PBD..... Polybutadiene

PBH..... High molecular weight polybutadiene
PBL..... Low molecular weight polybutadiene
PBM..... Low molecular weight cis/trans/vinyl polybutadiene
PISOP..... Polyisoprene
PPM..... Parts per million
PSI.....Pounds per square inch
RES.....Resonance
Rh..... Rhodium
RXN..... Reaction
SOL..... Solubilising
STA..... Simultaneous thermal analysis
TCM..... Trichloromelamine
TEMPO..... 1-oxo-2,2,6,6-tetramethylpiperidinium
TGA..... Thermal Gravimetric Analysis
THF..... Tetrahydrofuran
$\alpha TiCl_3$-$AlEt_3$..... Alpha titaniumtrichloride-triethylaluminium
UV/VIS..... Ultra violet/ visible
VAC.....Vacuum
WT.....Weight

ACKNOWLEDGEMENTS

I should like to take this opportunity to thank my supervisor Professor David Cole-Hamilton for all his helpful discussions, guidance and encouragement during my years at St Andrews. I enjoyed working in the unique environment he generated which was focused yet relaxed and friendly, caring not only about academic progress but also the personal development of his students. I should also like to comment, if I may, on his enthusiasm not only at the bench but also on the dance floor as exhibited at the International Symposium on Homogeneous Catalysis Dinner Dance in Princeton in August 1996, which confirmed that he is not only a great chemist but also a funky dancer! I am also grateful to Professor David Cole-Hamilton for the opportunity to present my work at two international symposia, i.e. University of Princeton and York, and also partaking in the exchange to University of Debrecen in Hungary, all were extremely enlightening.

My gratitude also goes to my industrial supervisor Dr Andrew Poole and ex-industrial supervisor Professor Mike Green for their helpful discussions and entertaining dinners both at the University and BP Chemicals Hull and Sunbry. Thanks must also go to BP Chemicals Ltd for funding my research project and the various conferences in which I participated.

I should also like to thank Peter Pogorzelec who made my stay in St Andrews extremely enjoyable with his interesting philosophies both in the lab and down the pub. A great measure of my gratitude must go to him for his helpful discussions and his sharing of various experimental techniques and last but not least for proof reading my thesis. In addition, thanks must go to Dr Douglas Foster for his advice on various experiments and the techniques involved.

I appreciated all the help and encouragement from all the technical staff of the chemistry department, in particular: Colin Smith for is speedy delivery of both ordered and broken glassware, Jim Bews for help with various computer problems, Melanja Smith for help with the NMR and Sylvia Smith for help with the Micro Analysis. I also enjoyed their humour which made coffee time stimulating.

Several friends have helped and encouraged me during my years at St Andrews: Debra Blyth, Leslie Sawers, Ivan Craigie, Oliver Brendel and Scott Marr who know how much I enjoy the cinema and theatre, especially the Ballet, Ian Wood and Henry Rae (whose humour is second to none) with whom I have enjoy many evenings at pottery classes, star gazing and down the pub drinking hot chocolate, Patricia Madden and Andrew Marr for taking me into their home for several weeks and ensuring I didn't miss any episodes of ER and Friends,

Diane Masson and Jukka Kujanpää for maintaining my sanity in the last few months, Pauline Mina and Henri Burns who know how much I enjoy dancing and finally Martina McGrady, Ivette Fred, Ruth Augustin, Leanne Burgin, Regina Chowdhury, Gabry Giugliano, Dony Margiotta and Linda Gowan flatmates that I had great fun cooking and socialising with. I should like to thank them all for their support and also for ensuring I got my daily fix of chocolate.

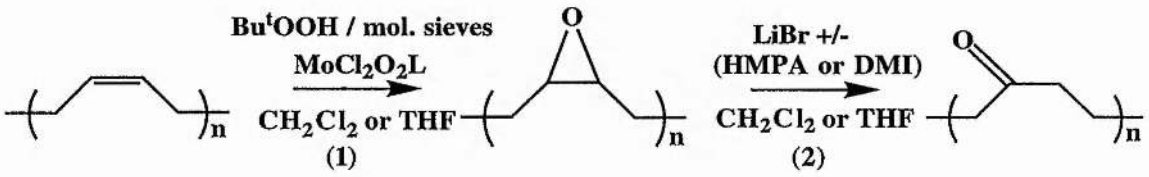
Finally, I should like to thank my research group past and present for an enjoyable time at St Andrews and especially for their support after the fire which destroyed my lab. I also enjoyed and will regretfully miss our regular trip to the pub for lunch on Friday, Christmas dinner, barbecues and the various parties throughout the year.

I should also like to single out Dr Charles Lindle, Joanne Rankin, Dr Steve Hagatta, Dr Barry Kaye and Dr Ahmed Iraqi for helpful discussions and listening to various presentations.

ABSTRACT

Our investigations into the synthesis of polyketones have involved the catalytic functionalisation of polydienes with particular emphasis on routes *via* a polyepoxide and a polyalcohol. Initially, a route *via* the polyepoxide was studied, in which polybutadiene (various micro structures and molecular weights) and polyisoprene were epoxidised (equation 1) in high conversion using a [MoO_2Cl_2 [(1R)-endo]-(+)-3(diethoxyphosphoryl) camphor] catalyst ($MoCl_2O_2L$) and subsequently isomerised to the polyketone using lithium bromide (equation 2), see Scheme 1.

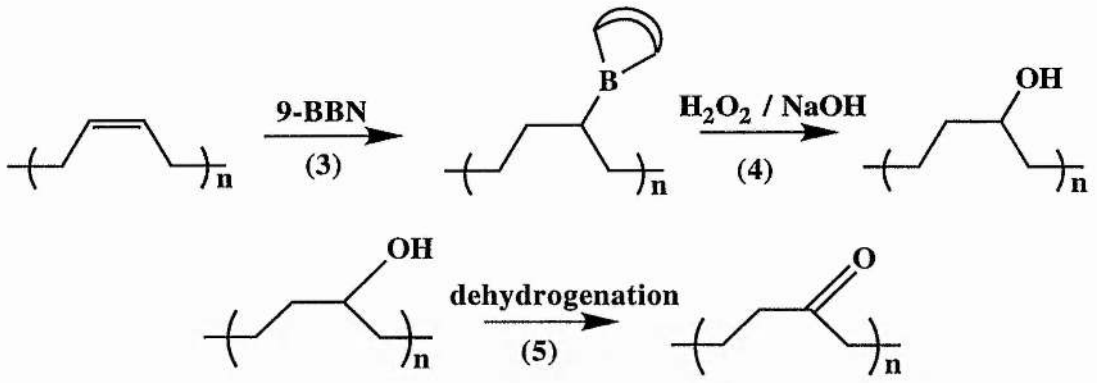
Lithium bromide requires a solublising agent in reactions carried out in dichloromethane, however this is not the case for reactions carried out in tetrahydrofuran as lithium bromide is readily dissolved in this solvent.



Scheme 1: The epoxidation of polybutadiene with Bu^{t}OOH using a molybdenum catalyst (1) and the subsequent isomerisation using lithium bromide with and without hexamethylphosphoramide.

Polybutadiene and polyisoprene can be easily converted to their respective polyepoxide. The backbone double bonds of the polydienes show from ^{1}H nmr 100% conversion to the epoxide with greater than 95% selectivity. The polyepoxides are easily purified after the removal of HCl (produced by the catalyst) as this causes crosslinking. Subsequent isomerisation of the purified polyepoxides show from ^{13}C nmr and ir that characteristic ketone units can be formed along with the ketal resonances attributided to brevicomin type moeties, formed from the reaction of a ketone with a neighbouring epoxide group.

Problems with the insolubility of the polyketone led to the preparation of a polyalcohol, *via* hydroboration using 9-borabicyclononane (equation 3) followed by oxidation using an alkaline solution of hydrogen peroxide (equation 4). The attempted dehydrogenation of the polyalcohol to give the resultant polyketone using various oxidants was studied, see Scheme 2.



Scheme 2: The hydroboration of polybutadiene with 9-borobicyclononane (3) followed by the oxidation to the polyalcohol using hydrogen peroxide and sodium hydroxide (4). And the subsequent dehydrogenation to the polyketone (5).

Conversion of the polybutadiene to the alcohol via hydroboration-oxidation using 9-BBN/NaOH-H_2O_2 showed by ^{1}H and ^{13}C nmr a 50% conversion of the backbone double bonds at a low temperature and 100% conversion at a high temperature. The microstructure of the resultant polyalcohol showed 1,4 : 1,5 : 1,6 segments in a 1:2:1 ratio, these different segment impart irregularity into the polymer chain and could consequently be carried through to the polyketone giving rise to lower crystallinity and a more processable polymer. Although various oxidants has been investigated for the dehydrogenation of the polyalcohol a suitable oxidant has not yet been found.

CHAPTER ONE

INTRODUCTION

1.0 INTRODUCTION

Polymeric materials which deliver high performance properties are in demand by technology today. Competitive trends and demanding applications continue to push for the production of materials with good engineering properties such as strength, stiffness, toughness, wear resistance and chemical resistance, especially those which operate at elevated temperatures. These properties and other product needs have provided opportunities for new and improved polymers.[1]

The incorporation of carbon monoxide into polyalkene polymers has been of considerable interest for many years. Initially, CO was used as a polymer building block because of its ability to impart some photo degradability to the polyalkene. This polymer (polyketone) can also be modified to form other functional polymers.[2]

Polyethene polymers containing small amounts of carbon monoxide have been shown to have properties similar to low density polyethene. However, copolymers with ethene / carbon monoxide (E/CO) compositions near 1:1 possess much higher melting points.[3] These copolymer compositions are random or perfectly alternating. The properties exhibited by the perfectly alternating E/CO copolymer are more useful than those of the random E/CO copolymer.

The perfectly alternating E/CO copolymer uses simple, inexpensive monomers and has a high density of carbonyl groups incorporated into a flexible polymer backbone, see figure 1.1, resulting in a potentially inexpensive crystalline polymer. This polymer exhibits a high melting point, stiffness, strength and process temperature, good solvent resistance and barrier properties which make it a suitable material for use in a wide range of applications.[1]

Until recently, an economical and viable synthetic route for the commercialisation of these desirable materials had proved difficult to achieve. The two main problems were firstly, identifying an effective catalyst and secondly, the polymer's apparent instability during processing. Given the recognised potential benefits to be obtained from these polymers, extensive research was undertaken to solve these problems. This research has led to the production of the first commercially available perfectly alternating polyketone this year, known as the Carilon material[1], with the first application being as a blade for a lawn mower.

1.1 PROPERTIES AND APPLICATIONS

This review will focus on the perfectly alternating copolymer, for example, the ethene carbon monoxide copolymer, as shown below.

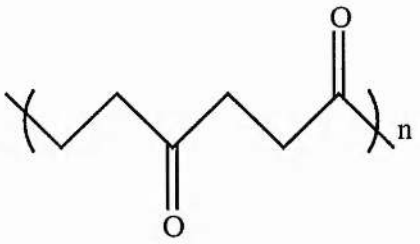


Figure 1.1: Perfectly alternating ethene carbon monoxide copolymer.

As a consequence of the structure, the polymer chains pack closely together resulting in a highly crystalline material. An assumed interaction between the carbonyl groups in each chain leading to the crystallinity of the material produce a unique, excellent and balanced set of properties not found in any other commercial thermoplastic polymers.

In particular they exhibit a superior combination of strength, stiffness and impact resistance especially over a broad range of temperatures and under high elongation. They also possess tribological properties; that is, friction and wear resistance, melt processability and chemical resistance as well as barrier properties to both hydrocarbons and gases.[1]

These properties place the polymers in a broad class of materials known as "engineering thermoplastics" which are utilised widely in industrial, automotive and electrical applications. For example, their chemical resistance makes them ideal for use as industrial pipes, pipe fittings, and as pumps and liners for chemical transfer and containment systems. This is due to the fact that they are not soluble in ordinary organic solvents and are not adversely plasticised by most reagents. They also benefit from their crystalline nature and the fact that they do not undergo hydrolysis.[1]

When comparing aliphatic polyketones with other suitable polymers for these applications it is observed that they possess much better properties.[1] For example, polyketones exhibit a better stiffness / toughness balance than polycarbonates, nylon 66, nylon 11 and polyacrylonitrile butadiene styrene, as it displays an impact energy of 54 ft-lb at a flexural modulus of 350 kpsi.

Similarly, the strength / elongation balance of the polyketone copolymer and terpolymer (ethene, propene and carbon monoxide polymer) is superior to nylon 66, nylon 11, polybutylene terephthalate, polypropene, low density polyethene and polycarbonate, and the copolymer is much stronger than the terpolymer which is a result of the crystallinity.

Wear resistance of the polyketone is extremely low compared with polyacetal and polyamide; it has been shown that the polyketone's weight loss over two weeks is almost negligible compared with the other two polymers using polymer-on-polymer gears.

Studies on the permeability of polyketones to gasoline and oxygen have shown that they have good barrier properties, when compared with other polymers such as teflon and nylon 12, for gasoline permeability, and polyethene terephthalate, and nylon 66 for oxygen permeability.

Good physical and barrier properties are also the result of the crystallinity of the polymer making the material ideal for use as automotive components, protective coatings and food and industrial packaging.

The awareness of the potential properties of such material stressed a need for an economical route resulting in extensive studies[4], [5], [6], [7], [8], [9], [10], [11] on suitable catalysts for polymerisation of carbon monoxide and alkenes and the polyketone itself.

1.2 THE SYNTHESIS OF POLYKETONES

The formation of polyketone via the copolymerisation of CO and ethene has been known since the 1940's. Brubaker[12] used a free radical initiated process to prepare copolymers of CO with a variety of alkenes in the early 1950's, and in the 1960's other radical copolymerisations were initiated by γ-radiation.[13] Both produced random copolymers.

However, development of coordination catalysts brought about the ability to produce alternating polymer structures of ethene and carbon monoxide. The first metal catalysed copolymerisation of E/CO was reported by Reppe and Magin[14] in 1951 using a nickel metal catalyst ($K_2Ni(CN)_4$) in water. Later in 1967 Gough prepared aliphatic polyketones using dichlorobis(*tert*-phosphine)palladium(II)[15] complexes under high pressures and temperatures. However, by the 1970's palladium based catalysts were improved so that they could be used under milder conditions. Fenton and Nozaki demonstrated that $Pd(CN)_2$ [16], [17], $Pd(PPh_3)_4$ [18], $Pd(PPh_3)_2Cl_2$ [18], $HPd(CN)_3$ [19] were effective catalyst for the copolymerisation of α-alkenes and carbon monoxide in a variety of solvents.

The polymers prepared, however, were not ideal as those with low molecular weights showed poor physical properties and high solubility in organic solvents. In contrast, the higher molecular weight polymer exhibited insurmountable processability, and stability problems and lack of significant thermoplastic properties.

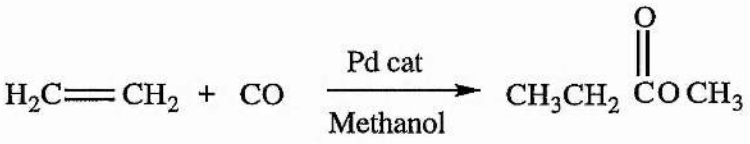
In the early 1980's, Hart demonstrated the melt processability of a polyketone[1] (after catalyst extraction and blending with other polymers) for the first time and showed that engineering properties were possible from a perfectly alternating copolymer. Sen then showed that cationic Pd(II) complexes of the type $[Pd(PR_3)_n(MeCN)_{4-n}](BF_4)_2$ [7], [8] were capable of copolymerising alkenes and carbon monoxide under significantly milder conditions than previously reported.[18]

In 1982, while conducting non-polymer related carbonylation research, Shell discovered a new class of efficient Pd(II) catalysts[20] capable of copolymerising carbon monoxide and ethene into a linear, perfectly alternating polyketone polymer of high molecular weight.

Described hereafter is the research developed, in effect, to produce a viable and economic synthetic route for the production of polyketones[21], [22], [23], [24] by optimising the use of palladium catalysts in the existing copolymerisation process. There is also an in-depth look at the preparation of the ECO polymer with reference to the reaction mechanism, catalyst composition and the polymerisation; initiation, propagation and termination steps. This will culminate with a look at the processability and stability problems associated with the polyketone materials and how recent advances have overcome such problems to make the polymer commercially successful.

1.3 DEVELOPMENT OF AN EFFICIENT PALLADIUM CATALYST

An efficient Pd catalyst for the copolymerisation of ethene and carbon monoxide was discovered by Shell[20], [25] in the early 1980's while working on the carbonylation of ethene in methanol to form methyl propionate, equation 1.1. The catalyst used to prepare methyl propionate was a cationic palladium complex precursor containing a weakly or non-coordinating anion and an excess of a monodentate phosphine ligand as shown in figure 1.2.



Equation 1.1: Carbonylation of ethene in methanol using a monodentate palladium catalyst to produce methyl propionate.

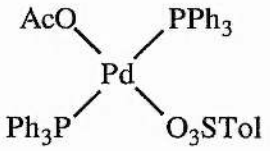


Figure 1.2: Catalyst for the preparation of methyl propionate: Palladium acetate with a monodentate ligand (PPh_3) and a labile anion (O_3STol).

Replacement of the monodentate ligand by a bidentate diphosphinoalkane of the general formula $Ph_2P(CH_2)_nPPh_2$ (figure 1.3) induced a large change in chemoselectivity of the catalyst and instead of methyl propionate, a white solid was observed which was later shown to be a perfectly alternating polyketone. The polymer had a melting point of 270°C and was virtually insoluble in every common organic solvent with the exception of hexafluoroisopropanol.

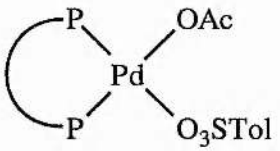
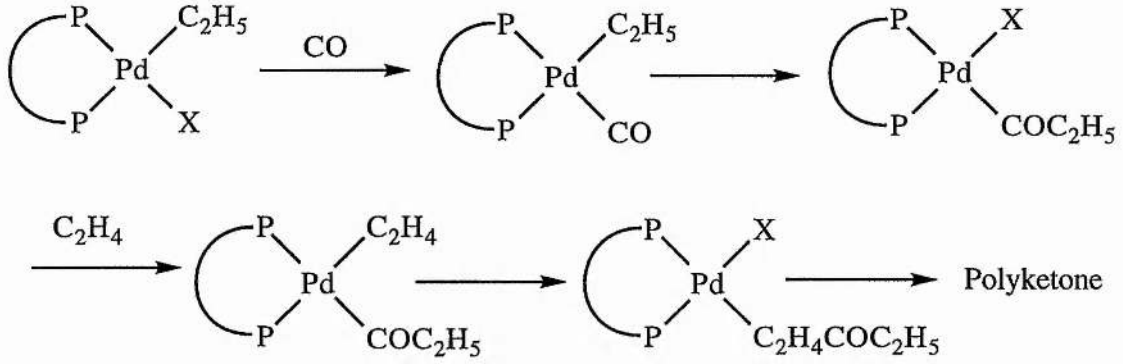


Figure 1.3: Catalyst for the preparation of perfectly alternating polyketones: Palladium acetate with a bidentate ligand ($Ph_2P(CH_2)_nPPh_2$) and a labile anion (O_3STol).

The catalyst was not only effective in producing the desirable polyketone and increasing the reaction rate but was also able to do so at a lower temperature and pressure than had previously been possible.

The preparation of methyl propionate involves only one insertion of ethene and one insertion of carbon monoxide and subsequent termination by methanolysis, it is therefore evident that the methyl propionate is the first product in the ethene/carbon monoxide series.

The excess monodentate ligand[26], [27] involved in forming the methyl propionate brings about rapid *cis/trans* isomerisation placing the empty fourth coordination site and the chain *trans* to one another and thus opposes further monomer insertion. Therefore, further insertion of ethene and carbon monoxide does not take place. This is not the case for the polyketone as the use of the bidentate ligand places the empty fourth coordination site and the chain *cis* to one another which permits subsequent insertion of ethene and carbon monoxide leading to chain growth. (equation 1.2)



Equation 1.2: Stepwise insertion of carbon monoxide and ethene into the Pd-alkyl bond to form a perfectly alternating polyketone.

Clearly, monodentate ligands when used in excess produce methyl propionate whereas bidentate ligands will invariably produce polyketones. The effect of the different chelating ligands used would suggest that the coordination of the chelating ligands to the metal centre is an important factor which influences the reaction mechanism, the rate of the reaction and may in some cases affect the product formed. This is supported by the dramatic difference in product when the monodentate is replaced by a bidentate phosphine ligand. Other components of the catalyst such as the metal centre and the counterion can also influence the aforementioned parameters, along with the addition of an oxidant and the solvent used.

The most effective metal centres for the copolymerisation are the late transition metals palladium, nickel and rhodium; however, palladium is the preferred metal centre.[28], [29]

The bidentate ligands employed are usually those which contain two atoms of sulphur, phosphorus and nitrogen as shown in figures 1.4, 1.5 and 1.6, for example, bithioethers[30], diphosphine[31] and bipyridine[32] as these are best capable of complexing with the appropriate metals.

General formula for the sulphur, phosphorus and nitrogen bidentate ligands:

Figure 1.4: Bidentate ligands of sulphur where R_{1-2} are optionally substituted alkyl groups and R is an organic bridge with at least two carbon atoms.

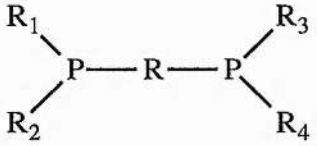


Figure 1.5: Bidentate ligands of phosphorus where R_{1-4} are aromatic groups substituted by one or more polar groups and R is an organic bridge of preferably three carbon atoms.

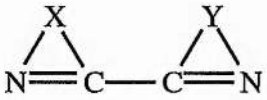


Figure 1.6: Bidentate ligands of nitrogen where X and Y are the same or different organic bridges of suitable three or four atoms of which there are at least two carbons.

Over the years, modification of bidentate ligands has led to a large increase in the number of this type of ligand, in an attempt to improve the reaction rate and molecular weight control. Generally, the bidentate ligand has been modified in three ways; by changing the chelating atom, the end groups or the bridging group, for example, the optimum chain length for a diphosphine ligand is $(CH_2)_3$ which gives the maximum reaction rate and the highest molecular weight.

1. The chelating atoms

This can either be sulphur, nitrogen or phosphorus as discussed above, all of which are capable of producing a perfectly alternating copolymer. Although the phosphorus is preferred both the nitrogen[33] and the sulphur are more resistant to oxidation and the sulphur ligands are simpler to make and therefore less expensive.[30]

2. End groups of the ligand

Addition of polar substituents on the aryl groups R^1-R^4 of the R^1R^2P-R^5-PR^3R^4 ligand increases the reaction rate.[34] The substituents may be in the ortho, para or meta positions with the ortho-position being preferred; for example, alkoxy groups at the ortho- and meta-position or a halogen at the para-position. The end groups R^1-R^4 in the

ligand can also be carboxylic acid groups which also gives rise to effective catalysts for the copolymerisation of ethene and carbon monoxide.

3. Bridging groups of the ligand

The reaction rate can also be increased by the addition of an alkyl or hydroxyl group to the centre carbon atom of the chain R^5 bridging the two phosphorus atoms or by the addition of groups such as $-C_6H_4-Fe-C_6H_4-$ [20], -RO- or -ORO- [31] where R is an alkylene group and -OH(C)R'- [35], where the R' = alkyl group of up to 6 carbons. The R_5 bridging group may be altered in length and bite angle. Both affect the molecular weight and the rate of insertion, for example the bidentate phosphine ligand could be 1,3-bis(diphenylphosphino)propane (dppp), 1,3-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(diphenylphosphino)butane (dppb), with dppp being preferred.[36]

Ligands of the type $R^1X=R=XR^2$ and $R^1X=R=XR^2R^3$ are also suitable for the copolymerisation of ethene and carbon monoxide.[37] The bridging R group is a hydrocarbon which is linked to X via a non-aromatic carbon-carbon double bond, R^1 is a monovalent hydrocarbon and R^2 and R^3 can be identical or different hydrocarbon groups. Alternatively, chiral ligands can be used for the production of optically active polymers, or a solid ligand bound to a carrier[38] (such as the polymer being formed) can be used to obtain polyketones free from catalyst residues. The average molecular weight of the polymer obtained is determined to a large extent by the average particle diameter of the solid carrier employed, polymers with a higher average molecular weight are obtained with catalyst compositions in which the dentate ligand is applied to a solid carrier with an average particle size larger than 500μm. Carriers used are generally porous and the catalyst is impregnated not only on, but in the carrier which will influence the molecular weight of the polymer.[39]

A counterion, in this case an anion, also plays an important role in the catalysis as it increases the rate of the reaction. Weakly or non-coordinating anions give the best results as they facilitate the access of the fourth coordination site on the palladium to the monomers. The anions can be introduced to the reaction via a Bronsted[40] or Lewis acid as the anion source during the reaction with palladium acetate. Although small traces of acid remaining in the polymer reduce the thermal stability of the polymer during processing, this can be avoided by using aluminoxanes $[(R^3R^4Al)_2O]_n$ or $[R^5AlO]_{n+2}$ instead of the acid.[41] The rate of the reaction in the presence of an aluminoxane maybe enhanced by the addition of a t-butyl aluminium compound.[42]

Another observed increase in the catalytic activity occurs when the anion used is of the form BXYZ where B is boron and X,Y and Z are ortho or para-chloro or bromo-phenyl groups, alternatively they maybe fluorine groups, for example, BF_4.[43]

The catalyst components may be added in situ or as a complex including the metal, ligand and anion; either way the result is the same. The catalyst may also be added to the reaction on a support such as a polymer. In particular a polyketone[44], [45] similar to that being produced, reduces the impurities from solvents used to add the catalyst.

An oxidant is added to the catalytic system as it assists in the regeneration of the active Pd species from precipitated palladium metal and as a result increases the reaction rate[40] and molecular weight. The reaction rate may also be affected by the solvent employed, which can be either water, or an aprotic solvent. The reaction can even be carried out under solvent free conditions in the presence of hydrogen or a trace of water.[25] In aprotic solvents such as alcohols the molecular weight is affected by the termination of the polymer via alcoholysis.[8], [46] Therefore, the molecular weight of the polymer will increase when small aliphatic alcohols are replaced by aliphatic ketones which will reduce the effect of alcoholysis.[47] The rate of the reaction and bulk density of the polymer will decrease, but are improved using an alcohol/ketone solvent mixture. No polymer is obtained when t-aliphatic alcohols are used by themselves, however, in the presence of other alcohols they are superior to any other alcohol solvent in preparing polymers of high molecular weight with good reaction rates.

The addition of hydrogen[48] and water[29] increases the reaction rate and reduces the molecular weight. For example, when hydrogen is added in the presence of tetra(aryl)bisphosphine ligand a low molecular weight polymer is obtained.[40] An increase in temperature, minor amounts of a hydride moiety [49] (e.g. metal hydrides or molecular hydrogen) and alkenyl substituted aryl groups lower the molecular weight.[49]

An in-depth study of the catalytic mechanism and the effect of the catalyst components has led to a better understanding of the copolymerisation of ethene and carbon monoxide. There are two schools of thought as to how the copolymerisation of ethene and carbon monoxide takes places. According to Sen and Drent (see review references page 9) a rational chain growth mechanism would involve alternate insertion of CO and alkene into the Pd-alkyl bond. They also believe that the spiroketal structure observed in the product is formed in tandem with the chain growth mechanism. In contrast, Consiglio believes that the propagation by a carbene species takes into account the formation of the spiroketal structure.[50]

The propagation, initiation and termination steps of the chain growth mechanism will be discussed and then compared to the carbene mechanism. In particular the role of the ligand and oxidant, the effect of the counterion, solvent system and growing polymer chain are highlighted as these are significant factors, as previously indicated, which influence the catalytic mechanism, the rate and the end product.

1.4 OVERALL REACTION MECHANISM

An outline of the proposed chain growth reaction mechanism from the study of the palladium catalyst in methanol is discussed below explaining the initiation of the catalyst by methanol, subsequent migratory insertion of ethene and carbon monoxide, and lastly, termination via methanolysis. In the case of propene there are two modes of insertion (1,2 and 2,1) in the Pd-acyl intermediates. High regioregular polymers have been obtained using arylphosphine ligands and non-coordinating anions in which repeated 1,2 insertion has been confirmed by end group analysis.[25]

Drent proposes that the initiation of the reaction with ethene takes place via reaction of the palladium complex with methanol to give a Pd-methoxy species (equation 1.3), carbon monoxide then coordinates and the anion is subsequently displaced (equation 1.4).

$$[L_2PdX_2] + MeOH \longrightarrow [L_2Pd(OMe)X] + HX$$

Equation 1.3: Generation of the Pd-OMe species.

$$[L_2Pd(OMe)X] + CO \longrightarrow [L_2Pd(CO)OMe]X$$

Equation 1.4: Coordination of carbon monoxide with displacement of anion (X).

The next step involves the migratory insertion of the carbon monoxide into the Pd-OMe bond to form a Pd-carbomethoxy species (equation 1.5), followed by the coordination of ethene (equation 1.6).

$$[L_2Pd(CO)OMe]X \longrightarrow [L_2Pd(C(O)OMe)X]$$

Equation 1.5: Migratory insertion of carbon monoxide into a Pd-OMe bond.

$$[L_2Pd(C(O)OMe)X] + C_2H_4 \longrightarrow [L_2Pd(C_2H_4)COOMe]X$$

Equation 1.6: Coordination of ethene with displacement of the anion (X).

The coordinated ethene molecule then inserts into the Pd-carbomethoxy bond to give the Pd-dimethylcarbomethoxy species (equation 1.7), which is terminated by methanolysis to give methyl propionate regenerating the Pd-OMe species (equation 1.8).

$$[L_2Pd(C_2H_4)COOMe]X \longrightarrow [L_2Pd(C_2H_4COOMe)X]$$

Equation 1.7: Insertion of ethene into the Pd-OMe bond.

$$[L_2Pd(C_2H_4COOMe)X] + HO\mathit{Me} \longrightarrow [L_2PdO\mathit{Me}X] + CH_3CH_2COOMe$$

Equation 1.8: Termination by methanolysis to yield methyl propionate and Pd-OMe

Alternatively, the polyketone may be formed if propagation takes place instead of termination. Chain growth may occur by coordination and insertion of ethene into the Pd-acyl bond[51] and carbon monoxide into the resultant Pd-alkyl bond[52] to give an alternating ethene carbon monoxide copolymer (equation 1.9).

$$[L_2PdC_2H_4COOMeX] \quad + \; n\,CO \; + \; n\,C_2H_4 \longrightarrow [L_2Pd(C_2H_4CO)_{n+1}\,OMeX]$$

Equation 1.9: Alternate insertion of ethene and carbon monoxide to form a polyketone.

This chain propagation process is in direct competition with the termination steps, which result from attack by methanol. Direct attack by methanol after ethene insertion results in the formation of an ethyl ketone end group (equation 1.10).

$$[L_2Pd(C_2H_4CO)_{n+1}\,OMeX] \quad + \; HO\mathit{Me} \longrightarrow [L_2PdO\mathit{Me}X] \quad + \; H(C_2H_4CO)_{n+1}\,OMe$$

Equation 1.10: Termination by methanolysis directly after ethene insertion to give a ketone end group.

The last two steps are very important as their relative rates determine the average molecular weight of the copolymer and the product distribution is governed by competition between insertion of a comonomer into the growing polymer chain and termination of the polymer chain by methanol.

If methanol attacks directly after carbon monoxide insertion then an ester end group is produced (equation 1.11 and 1.12).

$$[L_2Pd(C_2H_4CO)_{n+1}\,OMeX] \quad + \; CO \longrightarrow [L_2PdCO(C_2H_4CO)_{n+1}\,OMeX]$$

Equation 1.11: Insertion of carbon monoxide into a Pd-Alkyl bond.

$$[L_2PdCO(C_2H_4CO)_{n+1}\,OMeX] \quad + \; HO\mathit{Me} \longrightarrow [L_2PdHX] \quad + \; \mathit{Me}OCO(C_2H_4CO)_{n+1}\,OMe$$

Equation 1.12: Termination by methanolysis directly after carbon monoxide insertion to give an ester end group.

The Pd-OMe species would not be regenerated via this type of termination, instead, it is suggested by Drent[25] that the Pd-H is formed.

It is considered probable that a palladium hydride is also active for copolymerisation. However, the first step involves insertion of ethene into the Pd-H bond (equation 1.13) rather than carbon monoxide insertion into the Pd-OMe bond (equation 1.14).

$$[L_2PdHX] + C_2H_4 \longrightarrow [L_2PdCH_2CH_3X]$$

Equation 1.13: First Pd-H initiation step, insertion of ethene into a Pd-H.

$$[L_2PdOCH_3X] + CO \longrightarrow [L_2PdCOOCH_3X]$$

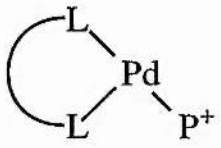
Equation 1.14: First Pd-OMe initiation step, insertion of carbon monoxide into a Pd-OMe

1.5 THE CHAIN GROWTH MECHANISM

A greater understanding of the propagation, initiation and termination of copolymers of ethene and carbon monoxide has been gained through the study of ketoester, diester and diketone end groups from soluble oligomer fractions of the polyketone.

The catalytic species utilised in these reaction is a d^8 square-planar cationic Pd complex $L_2Pd\ P^+$ where the L_2 is the bidentate ligand and P^+ is the growing polymer chain. (figure 1.7).

Figure 1.7:



The empty fourth coordination site may be occupied by solvent, anion, monomer or the carbonyl end group of the polymer chain all of which are usually weakly coordinated to the metal centre. Strongly coordinated groups would only inhibit chain growth by reducing the rates of insertion.[53], [54], [55] The competition for the vacant site is important as it affects the catalysis and explains the sensitivity of the system to the anion and solvent used.

1.5.1 PROPAGATION

The propagation of the copolymer is believed by Drent and Sen to take place via the alternate insertion of an alkene (ethene or propene) and carbon monoxide into a Pd-alkyl bond. Drent[25] suggested this mechanism from a study of the ethene/carbon monoxide copolymer and its chain ends, whereas, Sen[46], although his approach was similar to that of Drent, concentrated on the propene/carbon monoxide copolymer.

The catalyst systems used by Drent were neutral and cationic complexes respectively $[Pd(MeCN)_2(O_3STol)_2]$ and $[Pd(MeCN)_4](O_3SCF_3)_2$ combined with the 1,3-bis(diphenylphosphino)propane (dppp) ligand using methanol as the solvent. Sen focused on a cationic species $[Pd(Ph_2P(CH_2)_3PPh_2)(MeCN)_2](BF_4)_2$ using methanol-nitromethane as the solvent.

Two alternating propagation steps were proposed, the first is the migratory insertion of carbon monoxide into the Pd-alkyl bond[52] (equation 1.15 and 1.16) and the second involves the migratory insertion of the alkene into the Pd-acyl bond[51] (equation 1.17 and 1.18) from which a perfectly alternating structure is obtained.

1. Insertion into the palladium-alkyl bond

Equation 1.15:

$$Pd\text{—}Alkyl + CO \rightleftharpoons Pd\text{—}COAlkyl$$

Equation 1.16:

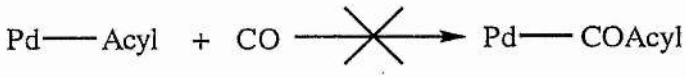
$$Pd\text{—}Alkyl + C_2H_4 \longrightarrow Pd\text{—}C_2H_4Alkyl$$

Under polymerisation conditions carbon monoxide insertion into the Pd-alkyl bond is rapid, reversible and has commonly been observed.[51] It is also favoured over alkene insertion as carbon monoxide is a better π-acid than alkenes and binds more readily to the palladium (II) centre.

Although alkene insertion into the Pd-alkyl bond is not as well known, when the reaction is carried out in the absence of carbon monoxide the same catalyst dimerises ethene to form butene. The formation of butene therefore indicates no insuperable thermodynamic barrier to alkene insertion into the Pd-alkyl bond. The formation of only dimers in the absence of carbon monoxide indicates that ß-H abstraction from the butyl intermediate is much faster than further insertion of ethene.[7], [8], [56] Alkene insertion is too slow to compete with the carbon monoxide, therefore carbon monoxide will insert into the Pd-alkyl rather than ethene.

2. Insertion into the palladium-acyl bond

Equation 1.17:



Equation 1.18:

Insertion of a molecule into the Pd-acyl bond is dictated by thermodynamics as indicated by a study of keto acyl complexes of Pd (II).[57], [58] The insertion of carbon monoxide into a Pd-acyl bond is thermodynamically uphill whilst insertion of an alkene into the same bond is thermodynamically down hill and therefore alkene insertion is observed. In most cases a vinyl ketone is formed via ß-H abstraction, however, in the case of norbornene the ß-H is inaccessible due to steric effects and stable derivatives of the complex are obtained.[59] An example is shown in figure 1.8.

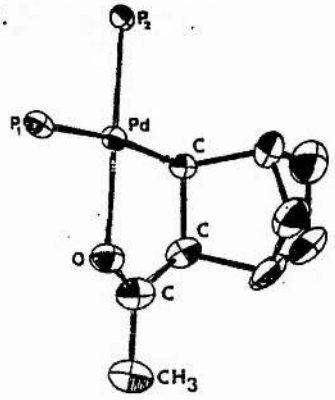


Figure 1.8: Crystal structure of [Pd $(PPh_3)_2(C_7H_{10}COCH_3)$]$(BF_4)$.

This crystal structure reveals important information regarding the alkene/carbon monoxide copolymerisation mechanism. The crystal structure agrees with the expected *cis* insertion which is required for chain growth, and shows that the organic fragment (norbornene + CO) acts as a bidentate ligand by coordination of the acyl oxygen. Similar results have been shown for a cyclopentadienyl insertion product. The different Pd-P bond lengths for the two PPh_3 ligands show that the coordination of the acyl oxygen is weak reflecting the different *trans* influences of the σ-bonded alkyl and the dative bonded acyl oxygen. The weakly coordinated acyl oxygen will displace easily allowing coordination of the monomers and their subsequent insertion.

Coordination of the acyl oxygen of the organic fragment supports the coordination of the ß-carbonyl at the polymer chain end to the palladium centre of the catalyst, discussed later, see page 32.

The kinetics of the reactions indicate that insertion occurs from a 4-coordinated intermediate, in which the alkene displaces the MeCN ligand. After the alkene has inserted into the Pd-acyl bond the oxygen of the carbonyl is coordinated back to the palladium to form a stable five membered ring.

Insertion of norbornene using a neutral $[Pd(PPh_3)(Cl)(COR)]$ complex is usually slower than when a cationic catalyst is used. The only difference between the two is that when the neutral compound is used the incoming alkene displaces the phosphine ligand prior to insertion. This is supported by the increased rate of insertion when a phosphine sponge is present.[59]

Requirements of the ligand displacement step mean that cationic weakly solvated Pd(II) compounds are preferred to the neutral analogues as displacement of weakly bond solvent molecule is easier than displacement of PPh_3 ligands. Alkene insertion into the Pd-acyl is the slowest step and therefore the rate limiting step, and although ß-H abstraction is a rare event dimerisation of ethene discussed previously (page 18) indicates that such a step is possible.

The evidence for the mechanism of copolymerisation via alternating insertion of CO in alkyl-palladium bonds and alkenes in acyl-palladium bonds provided by the crystal structure of $[Pd(PPh_3)_2(C_7H_{10}COCH_3)](BF_4)$ is further supported by the isolation and characterisation of the acyl- and alkylpalladium complexes, formed via successive CO and norbornadiene insertion reactions using a neutral acylpalladium complex ([Pd(Me)Cl(Ar-BIAN) containing a rigid Ar-BIAN ligand.[55] (figure 1.9)

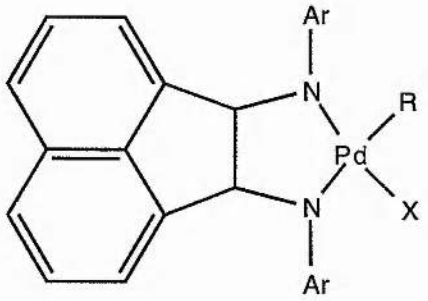
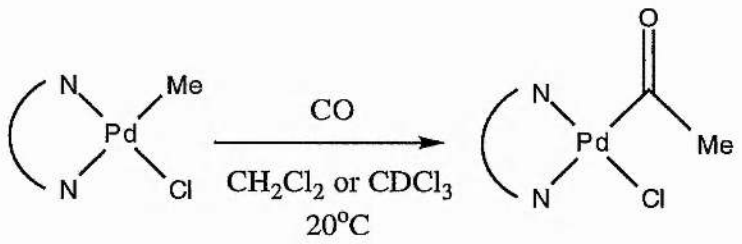


Figure 1.9: Neutral acyl palladium complex ([Pd(Me)Cl(Ar-BIAN)]).

The rigid Ar-BIAN ligands studied[55] exhibit an activating effect on insertion of CO and alkene in Pd-carbon bonds compared to other bidentate phosphorus and nitrogen ligands and also a stabilising effect on the Pd-acyl and Pd-alkyl complexes formed. In addition, the Cl anion is important in the stabilisation of the acyl complex as CO insertion of the norbornadiene

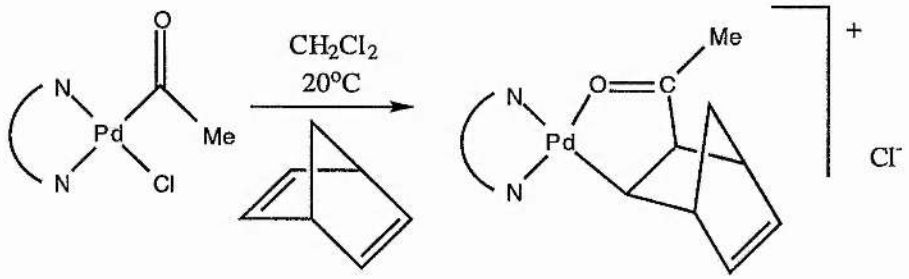
insertion complex $[Pd(C_7H_8C(O)Me)(Ar\text{-}BIAN)]SO_3CF_3$ was not observed. Both components of the catalyst have allowed the study of the acyl- and alkylpalladium complexes.

Formation of the neutral acyl palladium complex ([Pd(Me)Cl(Ar-BIAN) involves rapid carbon monoxide insertion into the methylpalladium complex to give the corresponding acetylpalladium complex. (equation 1.19)



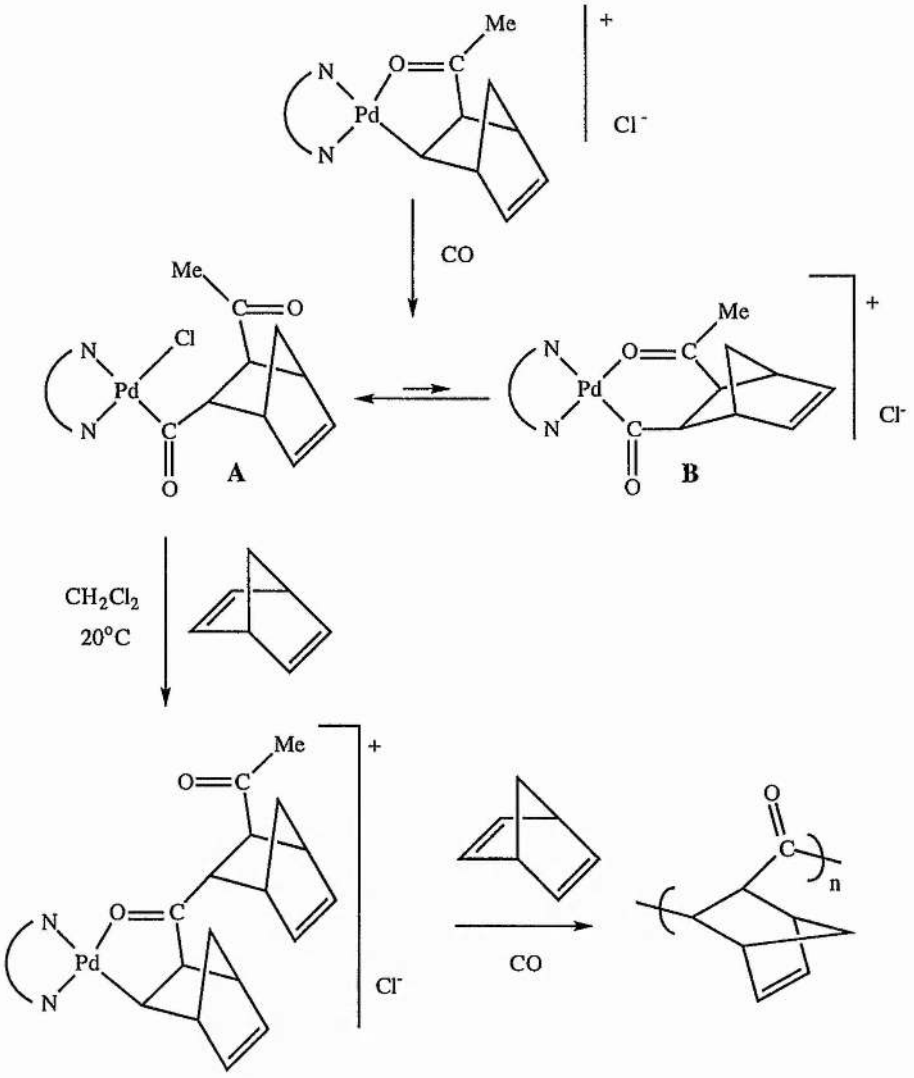
Equation 1.19: Formation of the neutral acylpalladium complex.

The acylpalladium complex then reacts with the strained alkene norbornadiene to give rapid quantitative formation of the insertion product, 5-membered palladacycle of norbornadiene. (equation 1.20)



Equation 1.20: Norbornadiene insertion into the neutral acylpalladium complex.

Successive insertions of CO and norbornadiene into Pd-carbon bonds then take place to form a polyketone. (scheme 1.1)

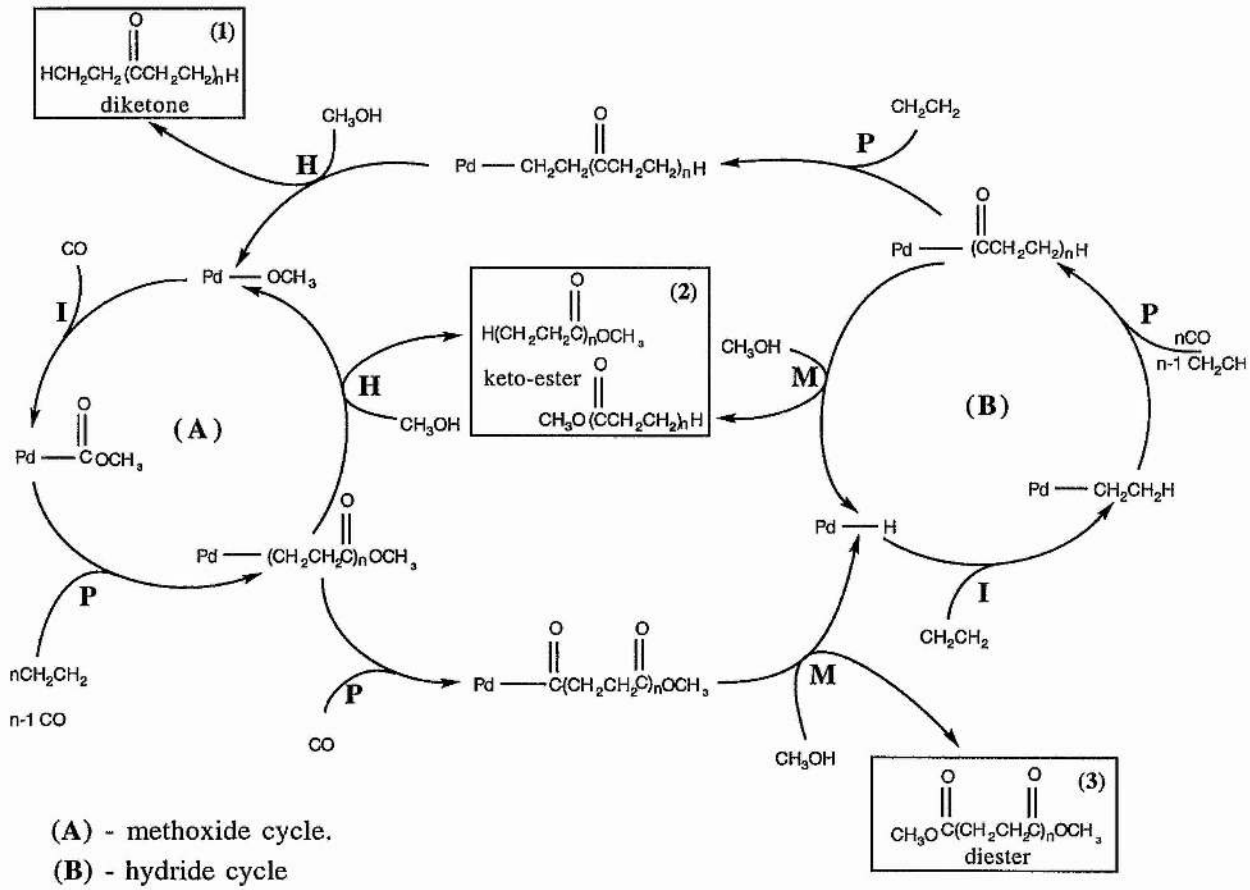


Scheme 1.1: Preparation of a polyketone via successive insertion of carbon monoxide and norbornadiene into the Pd-carbon bonds.

After the insertion of carbon monoxide in the 5-membered palladacycle of the norbornadiene inserted complex, a free coordination site (A) or a six membered palladacycle (B) is formed, which are both expected to result from thermodynamically unfavourable processes. The formed acyl complex then reacts quantitatively with norbornadiene to give an isolated alkyl complex containing alternating inserted CO and norbornadiene units. The isolation and characterisation of the acyl- and alkylpalladium complexes, formed via successive CO and norbornadiene insertion reactions, provide direct evidence for the stepwise chain growth in palladium catalysed CO/alkene copolymerisation.

1.5.2 INITIATION AND TERMINATION

Drent[25] and Sen[46] have shown the presence of diketone (1), ketoester (2) and diester (3) end groups of the oligomers and a small trace of vinyl end groups, determined by their relative initiation and termination mechanisms. At low temperature mainly ketoesters are prepared, however, at higher temperature (1), (2) and (3) are observed in a ratio of 1:2:1, suggesting that there are two initiation steps and two termination steps, as shown in scheme 1.2.



(A) - methoxide cycle.
(B) - hydride cycle
I - insertion
P - propagation
H - protonolysis
M - methanolysis

Scheme 1.2: The chain growth mechanism of a polyketone via alternate insertion of ethene and carbon monoxide.

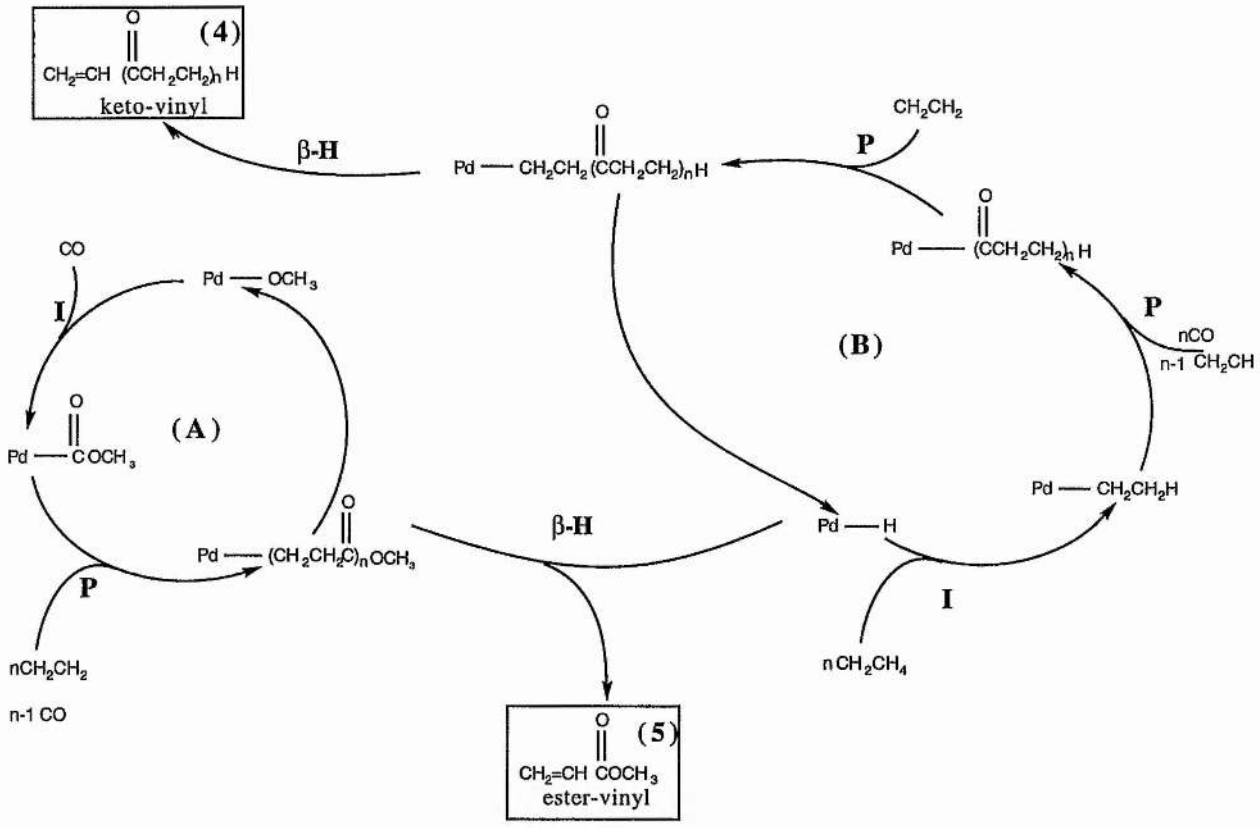
The first initiation step produces ester end groups (2, 3) in which the Pd-carbomethoxy is formed by the insertion of carbon monoxide into the Pd-methoxide or by direct attack of the methanol coordinated to the carbon monoxide. The second initiation step produces keto end groups (1, 2) by ethene insertion into the Pd-H bond followed by CO insertion in the resulting

Pd-alkyl which is rapid and reversible. The second ethene insertion is irreversible and therefore traps the acyl species which starts the growing chain.

The termination steps take place via protonolysis which involves the cleavage of a Pd-alkyl species to form a ketone end group and a Pd-OCH_3 species or by alcoholysis which involves the cleavage of Pd-acyl to form an ester group and a Pd-H species.

The reaction mechanism for the copolymerisation of ethene and carbon monoxide involves two main cycles (cycle A and B) which are made up of the previously mentioned initiation, propagation and termination steps. Both cycles produce keto-esters independently by rapid protonolysis and slow methanolysis initiated via Pd-OCH_3 or by slow protonolysis and rapid methanolysis initiated via Pd-H, but are linked by two cross termination steps which form the diester and diketone end groups, discussed above. At high temperatures more of diesters and diketones were obtained, indicating rapid transfer between cycles with comparable rates. At low temperatures, however, mainly keto-ester end groups were observed indicating that only one initiation or termination step is operating.[25] This may not be the case as the two routes could be operating independently, for example, the keto-ester maybe formed by cycle A or cycle B as shown in scheme 1.2. Product distribution alone is not sufficient to decide which cycle is responsible.

In addition, small quantities of keto-vinyl, ester-vinyl and keto-ether end groups have been observed in the oligomers.[46] The ester-vinyl groups are formed by the initiation of a Pd-OCH_3, however, the keto-vinyl groups are initiated from a Pd-H and both are terminated via ß-H abstraction from the Pd-alkyl. (scheme 1.3) The keto-ether end groups are formed from the initiation of the Pd-OCH_3 and termination via protonolysis of a Pd-alkyl species.



Scheme 1.3: The mechanism for the formation of keto-vinyl and ester-vinyl end group.

1.5.3 THE ROLE OF THE LIGAND

The preparation of the methylpropionate is very similar to that of the polyketone; in fact, it can be thought of as the initiation step and termination step of the polyketone with no intermediate propagation steps, as discussed earlier, see page 23.

There are two possible catalytic cycles, the methoxy cycle (cycle A) and the hydride cycle (cycle B) similar to that of the polyketone, however, the absence of the transfer cycle (i.e. crossover termination) suggests that only one cycle is working. Although it is possible that both cycles are operating in isolation.

A dramatic change in chemoselectivity of the catalyst is observed when the ligand in this reaction is changed from a monodentate phosphine ligand to a bidentate ligand resulting in the formation of a polyketone.[25]

The coordination of the phosphine ligands to the palladium metal centre plays an extremely important role in the formation of the end product, as the mechanistic route is dictated by the coordinated ligand and the resultant stereochemistry of the catalyst. For example, the monodentate ligand can be either *cis* or *trans* coordinated whereas the bidentate

ligand is always *cis* coordinated. Bidentate ligands, therefore, facilitate easy insertion of ethene, as the starting polymer and the empty fourth coordination site are *cis* to each other which is ideal for insertion reactions.(figure 1.10).

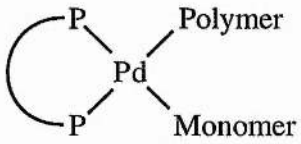


Figure 1.10: The bidentate phosphine ligand is coordinated in a *cis* position.

In contrast, the Pd-alkyl and Pd-acyl species prefer to be *trans* to the monodentate ligand for steric reasons and avoid the unfavourable Pd-P *trans* to the Pd-C. Insertion steps can only occur when the phosphine ligands are *cis* to one another.(figure 1.11)

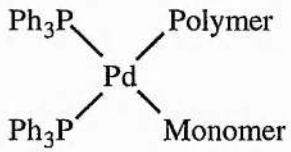


Figure 1.11: Monodentate phosphine ligands are *cis* coordinated.

Excess monodentate phosphine induces rapid *cis-trans* isomerisation. After the initial insertion, *cis/trans* isomerisation[26], [27] occurs and the polymer is situated *trans* to the empty fourth coordination site. Further insertion is opposed as the polymer and empty fourth coordination site are not *cis* to each other.(figure 1.12)

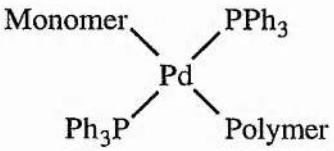


Figure 1.12: Monodentate phosphine ligands are *trans* coordinated.

The Pd-acyl is therefore terminated by alcoholysis to form the methyl propionate; this is also the case for Pd-OCH_3. If *cis-trans* isomerisation was suppressed, however, by removing excess phosphine or reducing temperature there is a higher tendency for the catalyst composition containing the monodentate phosphine ligand to form oligomers.[8]

1.5.4 THE ROLE OF THE OXIDANT

The catalytic activity of the palladium complex is enhanced by the addition of an oxidant. The rate of enhancement is 2-15 for diphosphine but >200 for bipyridine.[60] This enhancement is not due to faster propagation since chain length is not affected by (low concentration of) promoters, but due to the greater participation of the active species.[32]

The copolymerisation of carbon monoxide and ethene involves successive insertions into a Pd-OCH_3 or Pd-H bond, discussed earlier, see scheme 1.2 on page 23. Initiation via a Pd-OCH_3 forms ester end groups (cycle A) and a Pd-H forms alkyl end groups (cycle B) (both are rapid for alkyl alkenes) and termination via ß-elimination or methanolysis produces a Pd-H (cycle B), however, protonolysis forms a Pd-OCH_3 species which rapidly converts to a carbomethoxy species (cycle A).

Addition of low concentration of the oxidant to the reaction does not affect the chain length but results in a greater proportion of ester end groups which means that the oxidant causes more chains to start via a carbomethoxy species.[25]

If both the Pd-OCH_3 and the Pd-H species stay intact until they start a new chain then the addition of an oxidant would only affect the chain end groups (as discussed above) and not the rate of the reaction under these circumstances, but the fact that it does indicates that the Pd-H species can drop out of the cycle.

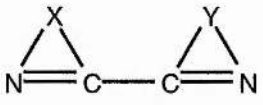
The Pd-H can be lost from the cycle due to decomposition to the $Pd^{(o)}$ (equation 1.21) and in the case of complexes containing nitrogen ligands, the $Pd^{(o)}$ may immediately lose it's ligand and precipitate as Pd metal (equation 1.22). In the case of aryldiphosphine ligands, they could combine with Pd^{2+} species to form a Pd_2^{2+} dimer, thus removing two Pd atoms from the catalytic cycles (equation 1.23).[53]

$$L_2PdH^+ \rightleftharpoons L_2Pd^{(o)} + H^+$$

Equation 1.21: Decomposition of the Pd-H species to $Pd^{(0)}$.

$$L_2Pd^{(0)} \rightleftharpoons Pd + 2L$$

where L =

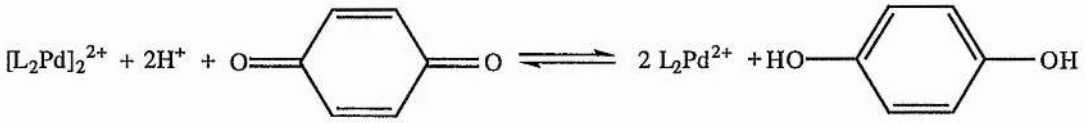


Equation 1.22: Precipitation of Pd metal from complexes with Nitrogen containing ligands.

$$L_2Pd^{(o)} + L_2Pd^{2+} \rightleftharpoons [L_2Pd]_2^{2+}$$

Equation 1.23: Formation of a Pd_2^{2+} dimer.

Each of these reactions reduces the rate of at which palladium hydrides can re-enter the catalytic cycle. Presumably, oxidants function by oxidizing some or all of these "dead ends" to Pd^{2+}, which can then immediately re-enter the cycle, as in equation 1.24.



Equation 1.24: Oxidzing Pd_2^{2+} dimer to Pd^{2+} species.

This implies that the Pd-H species is the main initiator in the absence of the oxidant which also suggests that the main termination step would be alcoholysis. The balance between the termination mechanism depends heavily on the ligand structure and the process conditions. Therefore, general conclusions cannot be drawn as the products will vary with reaction conditions and the catalyst composition.

1.5.5 GENERATION OF THE Pd-H AND THE EFFECT OF THE SOLVENT SYSTEM OF THE REACTION

The Pd-H species may be generated by two termination steps namely alcoholysis, which involves termination of the very first chain (equation 1.25) and ß-H elimination (equation 1.26), although the later step is not significant when the reaction is carried out in methanol.

$$Pd\text{—— acyl P} + CH_3OH \longrightarrow \text{polyketoester} + \text{Pd-H}$$

Equation 1.25: Termination by alcoholysis (P-polymer chain).

$$Pd\text{—— alkyl COP} \longrightarrow \text{polyketovinyl} + \text{Pd-H}$$

Equation 1.26: Termination by ß-H elimination (P-polymer chain).

Studies have shown that the termination rate is higher in methanol than in ethanol due to the steric bulk of the larger alcohol.(figure 1.13)[8]

$$CH_3OH > C_2H_5OH > C_3H_7OH > \text{etc}$$
Rate of Termination

Figure 1.13: Trend in termination with steric bulk of alcohol.

The smaller the alcohol the greater the termination rate, for example, in a study of t-butyl alcohol no oligomers were obtained. On the addition of methanol, however, the termination rate and the formation of oligomers increased. The rate of alcoholysis is also dependent on the nucleophilicity of alcohol employed.

As indicated above, these are clear pathways for the formation of Pd-H and / or Pd-OMe in alcoholic solvents, but such pathways are not available in aprotic solvents. Despite this, catalytic activity can be observed in some cases.

Reactions carried out in THF-nitromethane have shown an induction period before the copolymerisation begins, and the rate of the reaction is relatively slow compared to the reactions in protic solvents.[46] Addition of hydrogen, however, removes the induction period as the hydrogen is heterolytically cleaved to form the Pd-H initiator.(equation 1.27)

$$L_2Pd^{2+} + H_2 \longrightarrow L_2PdH^+ + H^+$$

Equation 1.27: Regeneration of Pd-H using molecular hydrogen.

Reactions carried out in D_2 instead of H_2 support this observation,[46] as indicated by Pd-D initiation confirmed by substantial deuteration of the terminated ethyl group. Deuteration of the

methene of the ethyl end group is also consistent with the rapid-reversible insertion of ethene into the Pd-D bond.

Water may also be added to the above reaction in the absence of hydrogen to generate the Pd-H species via a water-gas shift type reaction[61] (metal-H species are known to be intermediates).(equation 1.28)

$$L_2Pd^{2+} + CO + H_2O \longrightarrow L_2PdH^+ + CO_2 + H^+$$

Equation 1.28: Regeneration of Pd-H via a water gas shift reaction.

Deuteration of the terminal ethyl group of the ECO copolymer was observed when the reaction was carried out in THF-nitromethane in the presence of D_2O.

The Pd-H species can be generated, therefore, by ß-H elimination from the water-gas shift reaction, Wacker-type oxidation of ethene or hydrogen activation. Polyketone formation is observed when either water or hydrogen is added to the reaction components or if the reaction is carried out in a protic solvent. This observation and those previously mentioned confirm that the Pd-H species is generated by water-gas shift reaction or heterolytic hydrogen splitting and so water and hydrogen can be regarded as efficient initiators. Protonolysis and/or hydrogenolysis of palladium alkyls can therefore be thought of as efficient termination mechanisms.

1.5.6 ALTERNATION OF THE CO/ETHENE COPOLYMER

The two main considerations which can explain the perfect alternation of the ethene/carbon monoxide copolymer are; firstly, the competition for insertion between ethene and the carbon monoxide and, secondly, the coordination of the oxygen of the ß-carbonyl at the polymer chain end.

1. Competition between carbon monoxide and ethene

The competition between carbon monoxide and ethene for insertion can be observed by the absence of double monomer insertion. Double carbon monoxide insertion does not occur for thermodynamic reasons[57], [58] (equation 1.29), however, the absence of double ethene insertion which is exothermic is very interesting as it is known that ethene can form dimers using the same catalyst.[56], [7], [8]

$$L_2PdCOP + CO \not\longrightarrow L_2PdCOCOP$$

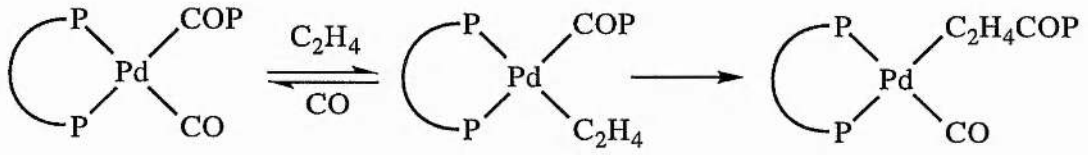
Equation 1.29: Double insertion of carbon monoxide.

Perfect alternation is achieved in the presence of low concentrations of carbon monoxide, although when the carbon monoxide has been consumed by the polymer, butene is then prepared.[25] Butene formation starts from the Pd-H in which ethene inserts twice and then terminates via ß-H elimination to regenerate the Pd-H species.(equation 1.30) The formation of butene shows that alkene insertion and ß-H elimination are intrinsically rapid.

$$L_2PdC_2H_4H + C_2H_4 \longrightarrow L_2PdC_2H_4C_2H_4H \longrightarrow \text{Butene} + L_2Pd\text{-}H$$

Equation 1.30: Double insertion of ethene to form butene.

The ethene-carbon monoxide copolymer prepared showed no double ethene insertion or ß-H elimination as the carbon monoxide coordinates more strongly to the Pd than ethene. The strong coordination of the carbon monoxide usually ensures that CO will be the next monomer to insert.[62] Although carbon monoxide coordinates more strongly to the Pd-acyl species insertion is thermodynamically unfavourable. Ethene and carbon monoxide are exchanging, so, although the equilibrium favours carbon monoxide coordination, the system waits for the ethene to coordinate and then rapid insert into the Pd-acyl bond occurs leading to chain propagation.(equation 1.31)



Equation 1.31: Coordination of carbon monoxide which waits till ethene coordinate and inserts.

This is why the alkene insertion step is regarded as the rate limiting step. The competition between the carbon monoxide and the ethene could be a factor which affects the reaction rate. There are a few unexplainable observations such as the rate of ß-H elimination and the overall reaction rate being lower than can be accounted for simply by the ethene/carbon monoxide competition.

2. Coordination of the ß-carbonyl of the polymer chain

Coordination of the ß-carbonyl of the polymer chain end will affect the formation of the copolymer, the result being a strictly alternating structure. After insertion of ethene the oxygen of the ß-carbonyl coordinates to the Pd acting as a chelating ligand forming a stable 5-membered ring species. (figure 1.14)

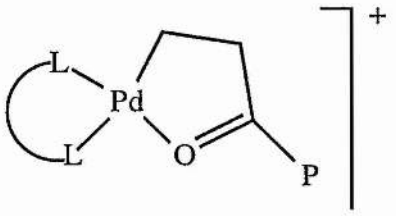


Figure 1.14: Stable 5-membered ring due to coordination of the ß-carbonyl of the polymer chain end.

The main driving force for the chelate formation is probably the electrostatic interaction between the positive Pd and negative oxygen of the carbonyl group. The internal coordination of the polymer may affect the propagation steps. The stabilisation by the chelate formation should increase the exothermicity of the alkene insertion into the Pd-acyl. The fourth coordination site is blocked by the polymer/Pd chelate, therefore the next monomer has to displace the chelated carbonyl group, which increases the insertion barrier. Displacement of the carbonyl group by ethene is difficult as the alkene coordination to the Pd is too weak and therefore the alkene faces the highest barrier to insertion.

Alternatively, carbon monoxide binds strongly to the Pd and requires less space than the alkene to coordinate. The carbon monoxide more readily displaces the carbonyl group and inserts to form a less stable 6-membered ring where the carbonyl group is delta to the Pd.(figure 1.15)

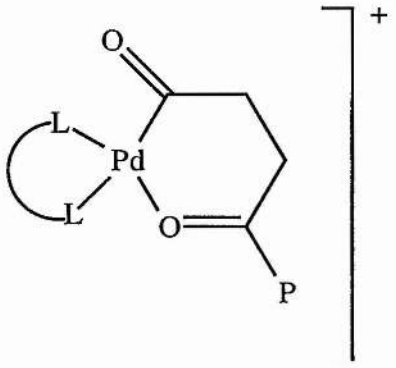


Figure 1.15: Unstable 6-membered ring due to insertion of carbon monoxide which allows easy insertion of ethene.

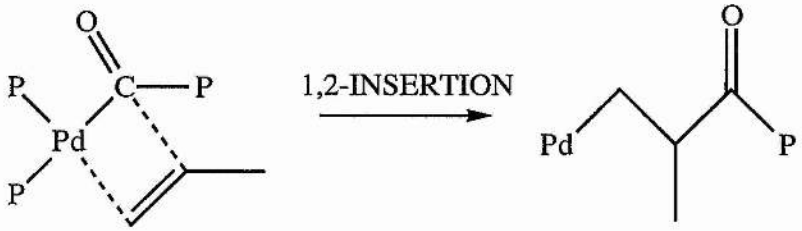
Ethene is readily able to displace the carbonyl group in the unstable 6-membered ring system and insert to give the stable 5-membered ring. The chelate effect will also slow down ß-H elimination as the ß-H has to approach the Pd and is inhibited by the coordinated carbonyl group δ to the metal centre chain end.

The chelate effect also imposes a *cis* environment when monodentate ligands are used, explaining the chain propagation and strict alternation of the polymer with monodentate ligands.[7], [8]

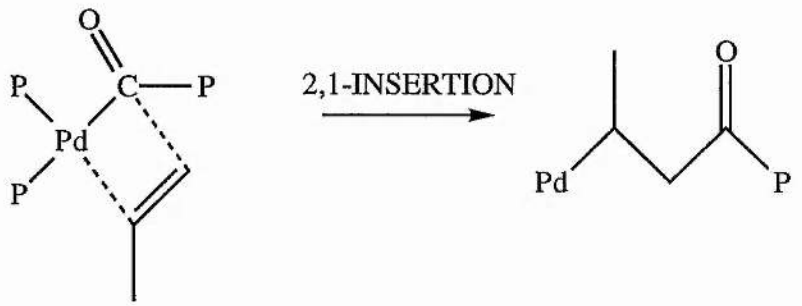
Essentially, the mechanism for the formation of the ethene / carbon monoxide copolymer involves internal coordination of the polymer chain end. Double carbon monoxide insertion is prevented thermodynamically, whereas carbon monoxide and ethene competition prevents double ethene insertion. The architecture of the polymer assists its own formation through the chelating of the carbonyl group δ to the Pd metal centre.

1.5.7 STEREO- AND REGIOREGULARITY OF THE PROPENE CARBON MONOXIDE COPOLYMER

The regio- and stereochemistry of the polyketone copolymer varies when higher alkenes are employed, as they can insert into the Pd-acyl species in a 1,2 or 2,1 fashion. This will determine the regiochemistry of the end polymer, which will be either regioregular or regioirregular. If the polymer is regioregular then the insertion will taken place via 1,2 or 2,1 insertion, although it is difficult to determine from the end product which has taken place.(equation 1.32 and 1.33)



Equation 1.32: 1,2-insertion of propene into a Pd-acyl bond.



Equation 1.33: 2,1-insertion of propene into a Pd-acyl bond.

A centre of chirality is created, for both regioinsertion modes, in each monomer unit in the polymer, as the regioregularity induces a direction in the chain. Atactic (random) , isotactic

(figure 1.16) and syndiotactic structure (figure 1.17) would result if a 1,2 or 2,1-regioregular propagation takes place. The isotactic alkene/carbon monoxide polymer is a rare example of a man-made optically active polymer synthesised from achiral monomers of which there are few.

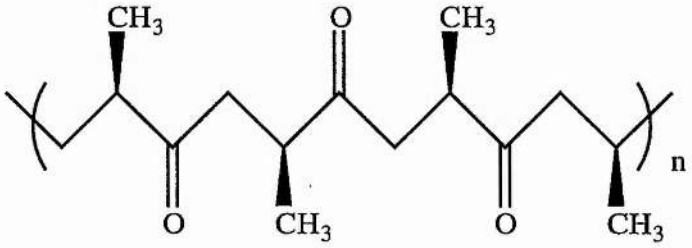


Figure 1.16: Isotactic propene carbon monoxide copolymer.

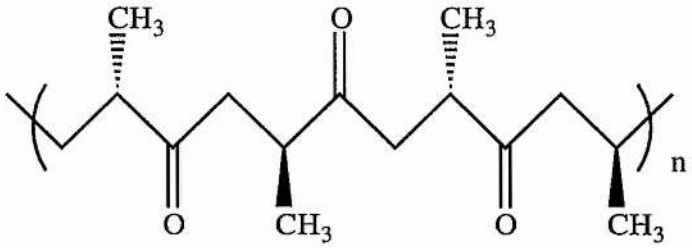


Figure 1.17: Syndiotactic propene carbon monoxide copolymer.

An understanding of the factors which govern the regio- and stereocontrol of α-alkene insertion in palladium (II)-acyl intermediates has been gained from a study of the same elementary steps found in hydroformylation and hydroacylation as in the copolymerisation when using a polyketone catalyst.[63]

Regioselectivity of propene carbon monoxide copolymerisation is determined by nmr, in which the two possible propene insertions 1,2 and 2,1 are shown to proceed with a relative frequency of 3:1 as indicated from the intensity ratio of the resonances. Catalysts containing aryl phosphine ligand have been shown by nmr to produce only a modest regioregularity of about 75%. This is confirmed by the absence of a sharp melting point for the polymer. Much higher regioregularity, however, can be achieved if the aryl phosphine ligand employed is replaced by an alkyl phosphine ligand, particularly in combination with a non-coordinating anion. Well defined melting points obtained for these polymers of 165°C and 260°C result in a 94% and 99% regular product respectively.

A regioregular chain end, which contains a centre of chirality, as indicated above, could impose an enantioface-dependent steric limitation on the incoming alkene. If this is the case then the regioregularity of the polymer chain and the enantioface selection in alkene insertion into the Pd-acyl intermediates could be related. High melting point and small line widths in the ^{13}C nmr confirm the presence of some degree of stereoregularity for polymer produced using bis-(diisopropyl-phosphino)propane (dippp).[24]

A similar correlation between stereochemical control and induced regioregularity is suggested by the analysis of CO/propene copolymers produced using chiral aryl phosphine ligands. A considerably increased head to tail enchainment of more than 90% is observed for these polymers, compared with the 75% observed with polymers produced with the achiral dppp ligand. Consiglio[64] and Sen[65] have observed virtually complete head-to-tail enchainment for polymers produced using chiral phosphine ligands and established by nmr that they have a higher degree of stereochemistry.

1.5.8 CHAIN GROWTH MECHANISM INVOLVING A CATIONIC PALLADIUM CARBENE SPECIES

Copolymers containing ketal repeat units were first reported by Van Doorn[66], and subsequently have been studied by Consiglio[50] and Wong.[67]

Consiglio observed a spiroketal structure when producing styrene/propene and carbon monoxide copolymers.(figure 1.18)

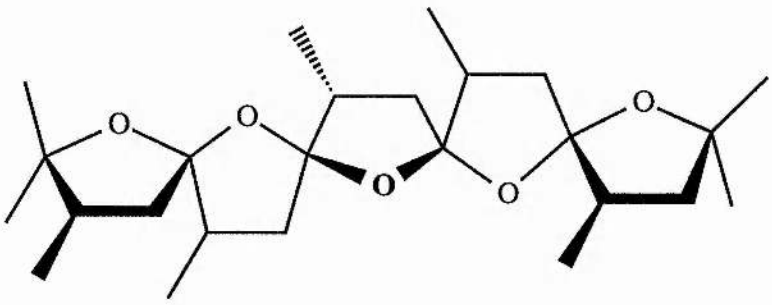
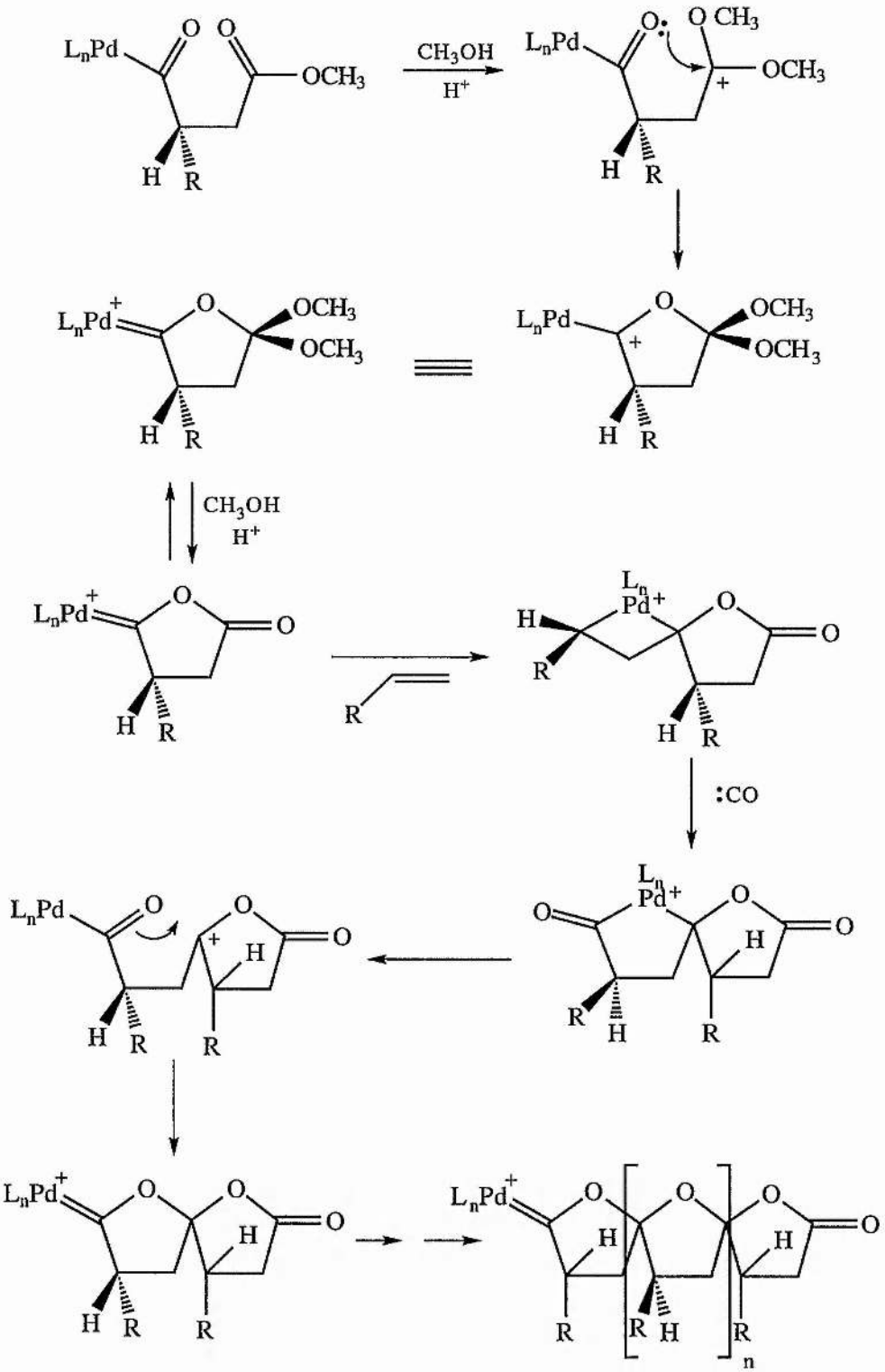


Figure 1.18: Polyspiroketal

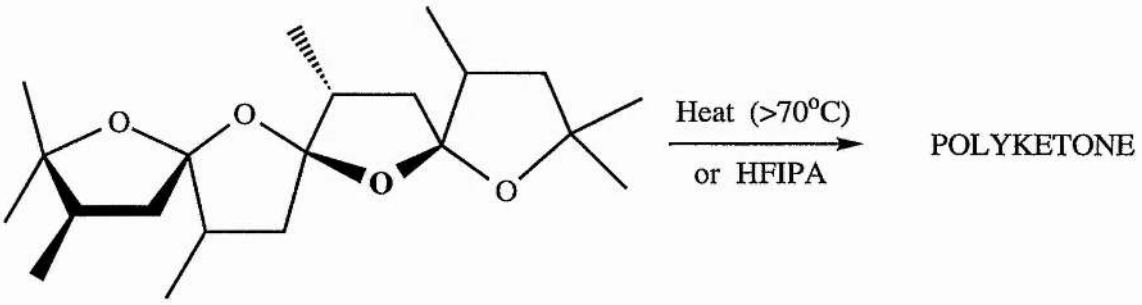
Consiglio believes that the chain growth mechanism involving alternate insertion of alkene and carbon monoxide into a Pd-alkyl bond is not consistent with the products formed. And, although no mechanistic study has been carried out, he proposes an alternative mechanism that involves the propagation via a cationic palladium carbene species as shown in the scheme 1.4.



Scheme 1.4: The mechanism for the chain propagation via a palladium carbene species.

Drent has investigated this work[24] and observed that the previously obtained alternating polyketones shows 70-90% spiroketal structures in the solid state nmr at room

temperature before their workup with HFIPA. The spiroketal structure is converted to the ketone at an onset temperature of 70°C and does not revert back to the spiroketal on cooling. Therefore, both heating and dissolution in HFIPA causes the spiroketal structure to open irreversibly to form the ketone structure suggesting that the spiroketal structure is formed during the catalytic chain growth.(equation 1.34)



Equation 1.34: Ring opening of the spiroketal by heat or dissolution.

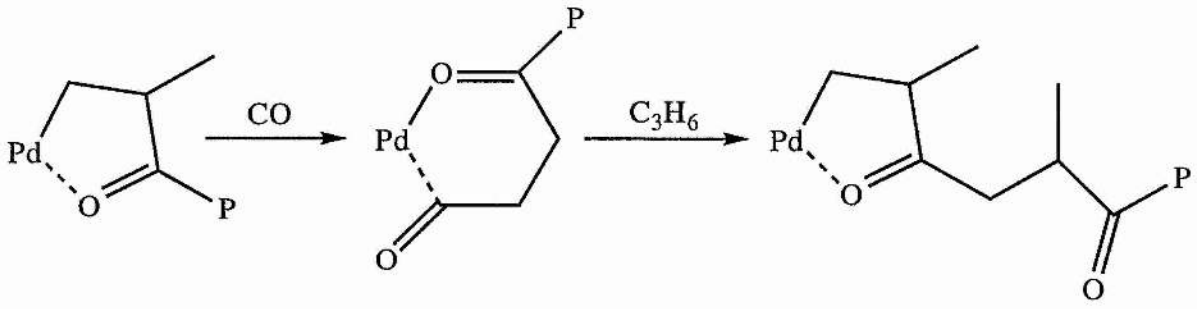
1.5.9 TANDEM MECHANISM FOR POLYSPIROKETAL FORMATION

In this alternative to Consiglio's carbene mechanism, the spiroketal formation could proceed "in tandem" with the classical chain growth mechanism.[24] Nucleophilic attack of the Pd-alkyl by a hemiketal OH group is simplified by internal coordination of the ß-carbonyl group of the polymer chain end to the palladium metal centre. An alcohol is a poorer donor than a carbonyl group; therefore, internal coordination at the alkyl stage is weakened allowing the next carbon monoxide to insert.

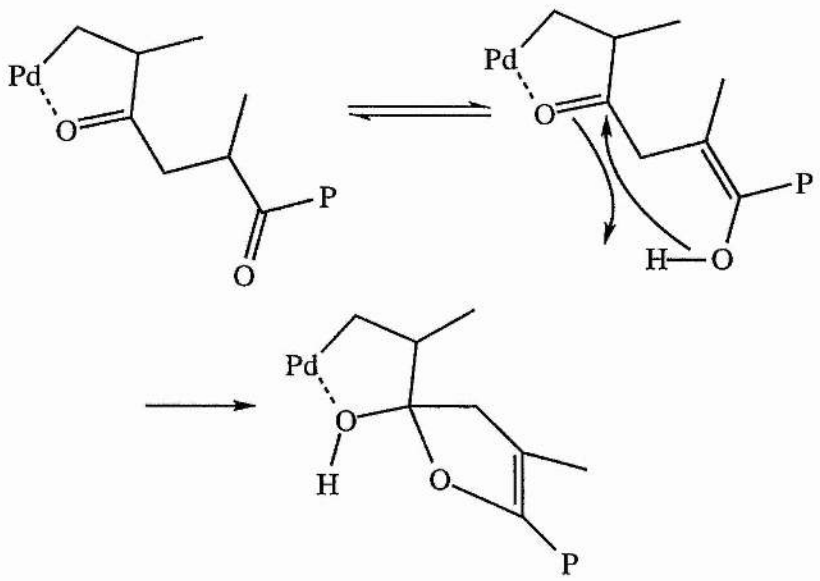
Polyspiroketal formation could start either by enolisation (2) or by attack of external methanol (3), as shown scheme 1.5. Since in the alternate insertion scheme polyketone propagation still occurs by the original mechanism, termination could also occur by the same route as that for the normal polyketone. For example, ß-elimination and protolysis could occur both before and after the alkyl group has isomerised to the spiroketal.

Scheme 1.5: A tandem mechanism for the formation of spiroketals with the chain growth mechanism via the insertion of ethene and carbon monoxide.

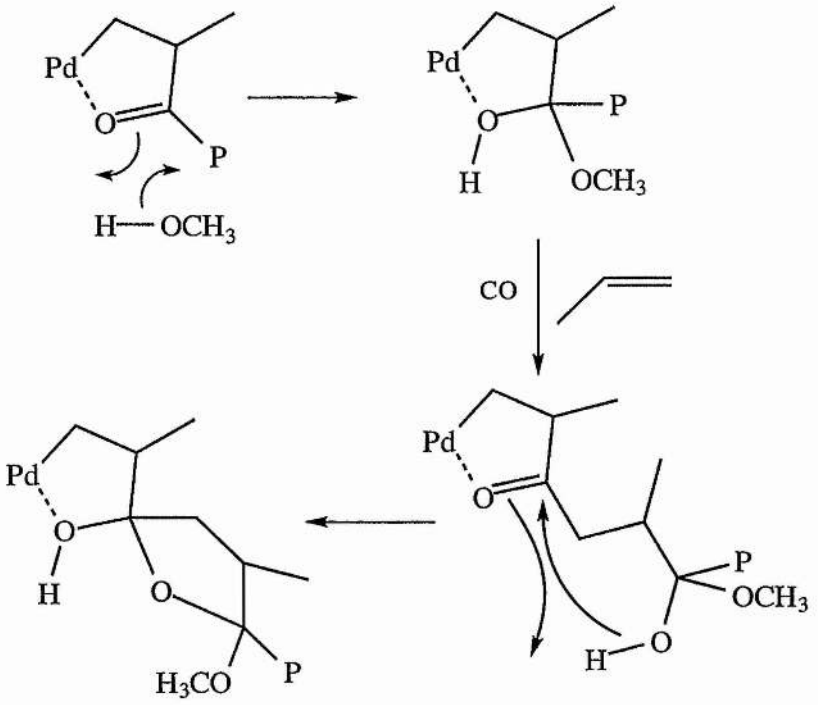
(1) normal propagation:



(2) Enolisation

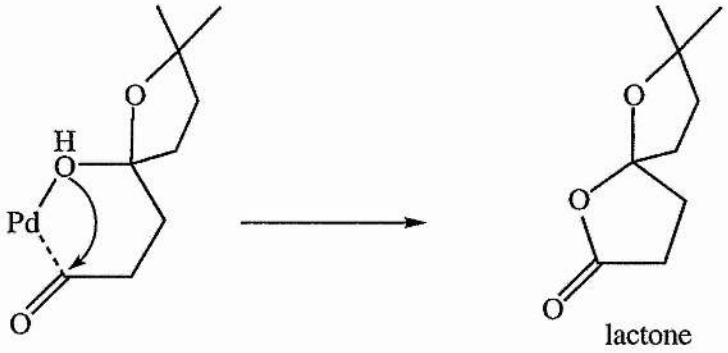


(3) Attack by methanol

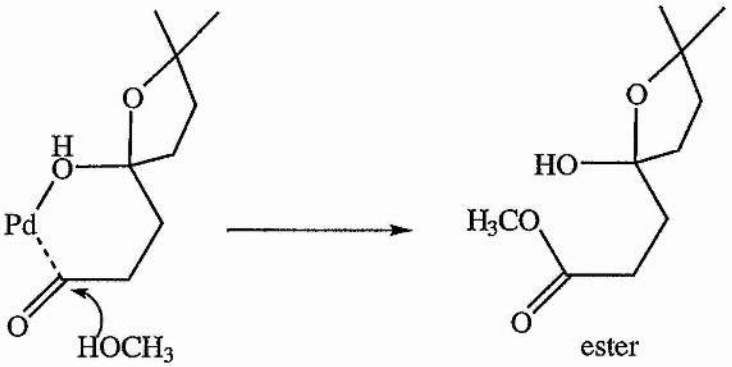


Consiglio[50] suggested a propagation mechanism involving carbene intermediate to explain polyspiroketal formation and the presence of lactone end groups (scheme 1.4). However, there is no mechanistic information to support this hypothesis. Since spiroketal and polyketone structure are so close in energy for α-alkenes/CO copolymers, conditions (solvent, temperature) can shift the equilibrium from one to the other. Polyketone/polyspiroketal isomerisation is catalysed by both acids and bases, but could be slow in the absence of any catalyst. Therefore, it is dangerous to draw conclusions about the mechanism of polyspiroketal formation from characterisation of the polymers obtained.

Drent[24] also suggests that the observation of both ester and lactone end groups is in accordance with an oxidative carbonylation mechanism, stoichiometrically based on the end groups of the polymer. Such oxidative carbonylation was also observed in ethene copolymerisation with carbon monoxide utilising the same catalyst and oxidant. The lactone end groups (equation 1.35) can be considered as arising from an intramolecular variant of the methanolysis termination step that normally produces ester end groups.(equation 1.36)



Equation 1.35: Formation of lactone end groups.



Equation 1.36: Formation of ester end groups.

1.6 STABILITY AND PROCESSABILITY OF POLYKETONES

The commercialisation of the polyketone was limited not only because of problems with its synthesis but also due to problems with the stability of the polymer during processing.[1] The simplest member of the aliphatic polyketones series is the ethene/carbon monoxide alternating copolymer, an engineering thermoplastic with a very attractive set of properties as discussed earlier (see page 7), but which exhibits significant processing problems due to its melt stability. As previously discussed (see page 7), the regular structure of the ethene/carbon monoxide polymer chains pack very close together resulting in a highly crystalline material with a high melting point.[3] (figure 1.19)

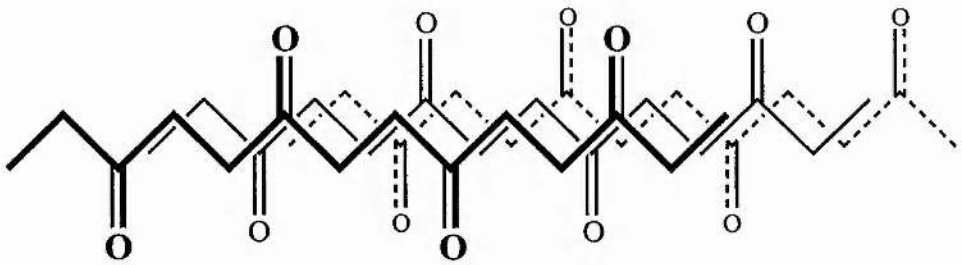


Figure 1.19: Close packing of the polyketone chains.

Such a material is ideal for many engineering applications due to its physical, mechanical, electrical, chemical and tribological properties.

Unfortunately, however, the decomposition temperature is very close to the melt temperature and as a result the polymer crosslinks on melting. The crosslinked polymer produced loses its much sought after engineering properties. It is also lacks solubility in hexafluoroisopropanol (one of the few solvents which dissolve the polyketone) and any melt endotherm in the DSC. Attempts to improve the processability by lowering the molecular weight, chemically modifying the polymer, or adding plasticisers were not successful.[1]

Initially, Hart demonstrated melt processability of the polyketone by extracting Pd catalyst residues from the polymer and blending polymer produced with other polymers such as styrene/acrylonitrile copolymer, showing that engineering properties were possible. Unfortunately, such extractions were uneconomical as they were not only time consuming but expensive to effect.

However, recent developments in the catalyst used for the copolymerisation of alkenes and carbon monoxide has resulted in an economically viable material known as aliphatic polyketones.[25] The active catalyst is based on a Pd centre, bidentate ligand and a non-coordinating or weakly coordinating anion. The main difference between this catalyst and others previously used to prepare polyketones is the substitution of monodentate ligands for bidentate ligands. The new catalyst not only assists in the preparation of perfectly alternating copolymers, but also increases the polymerisation rate markedly so that the level of catalyst

required is significantly reduced, making production of the new processable polyketone cost effective and consequently leaving fewer impurities in the polyketone produced. The amount of catalyst left in the polymer is now in ppm rather than in percent. Therefore, the removal of the catalyst after the polymerisation was no longer required which made the process more economical and improved the processability of the polymer product.

Although the extraction of the impurities was no longer a problem, the instability of the polymer during processing remained a problem. It became apparent that this was due to the crystallinity of the polyketone. Therefore, it was thought that the way forward was to alter the crystalline nature of the material but not completely as the crystallinity was responsible for many of the polyketone's enviable properties. In order to alter the molecular structure, a second alkene monomer was introduced, such as propene, which substitutes randomly for ethene to produce a terpolymer.[25]

The role of the second alkene in the terpolymer is to disrupt the packing to the polymer chains and consequently reduce the crystallinity and the melting point. This optimises the temperature range within which the polymer can be processed and further improves the polymer's resilience and flexibility with out adversely affecting any of the desirable properties outlined above.

CHAPTER TWO

EPOXIDATION

2.0 INTRODUCTION

It has been shown that the problem with the polyketone's processability and stability was only solved when the polymer backbone was altered to disrupt the packing of the polymer chains.[25] In this work we have investigated the preparation of polyketones via the modification of polydienes to assess what effect an additional carbon atom between the carbonyl groups would have on the end products.

Unsaturated polymers, especially diene polymers, are ideal for chemical modification because of the availability of the parent material and reactivities of the double bond in the polymer chain. Novel polymers obtained by chemical modification of existing polymers are generally inaccessible, uneconomical or difficult to synthesis by conventional polymerisation techniques.

Our aim is to synthesise polyketones with structures that are slightly different (less regular) from those of the ethene-carbon monoxide copolymer and investigate the properties that might be obtained from polyketones with more carbon atoms between the carbonyl groups in the polymer backbone, for example, the diagram below shows a polyketone with carbonyl groups in a 1,4, 1,5 and 1,6-position. (figure 2.1)

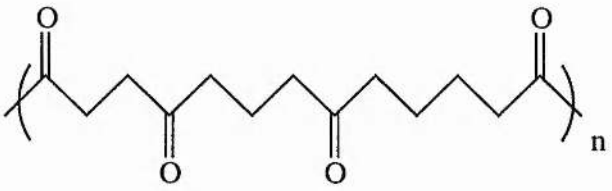


Figure 2.1: Structure of desired Polyketone:

In principle the products can have micro structures that are easily controlled and the functional groups of interest can often be introduced in a highly selective manner.

An obvious route to the above polyketone would involve catalytic functionalisation of polybutadiene with particular emphasis on routes via the epoxide and alcohol. The position of the carbonyl group relative to the initial double bond is not controlled, hence the irregular position of the carbonyl group shown in the diagram above. It has recently been shown that polyketones can be prepared by the modification of polybutadiene[68] (containing *cis/trans* and vinyl groups). In addition, polyalcohols have been prepared by hydroboration-oxidation reactions where the 1,5 hydroxyl group spacing dominates over 1,4 and 1,6 spacings.[69], [70] This irregularity if carried through to the polyketone would disrupt the packing of the polymer chains reducing the crystallinity.

The close packing of the ethene-carbon monoxide polymer chains results in a highly crystalline structure which generates a high melting point. This melting point is unfavourably close to the decomposition temperature of the polymer and therefore difficulties in processing

are encountered, as discussed above. In industry this problem is alleviated by introducing some propene into the polymer backbone which produces some irregular methyl group branching within the polymer chain. The irregularity within the terpolymer backbone disrupts the packing of the polymer chains reducing the crystallinity and the melting point resulting in a more processable polymer.[25] Polyisoprene was also investigated as this is similar to polybutadiene and in addition has pendant methyl groups, which will enable a comparison with the terpolymer.

This additional carbon atom in both diene polymers may also impart an increase in flexibility and irregularity to the polymer chain, consequently reducing the crystallinity and the melting point, hence creating a more processable polymer.

2.1 EPOXIDATION OF POLYBUTADIENE

2.1.1 SYNTHESIS OF POLYBUTADIENES

1,4- and 1,2-polybutadienes are mainly prepared from the free-radical emulsion polymerisation of 1,3-butadiene.[71] In the case of the 1,4-polymerisation, there exists the possibility of obtaining two geometrically isomeric polymers, 1,4-*cis* and 1,4-*trans* The microstructure of each polymer unit is shown in the diagrams 2.2-2.4 below:

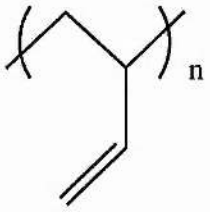


Figure 2.2: 1,2-polymer

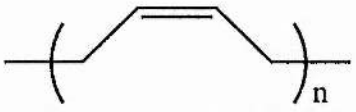


Figure 2.3: 1,4-*cis*-polymer

Figure 2.4: 1,4-*trans*-polymer

During polymerisation, the polymer chain length increases and branching may also occur at double bond sites in the linear chain, increasing the molecular weight of the polymer.

To avoid this, mercaptan transfer agents are generally used to cut down the molecular weight and prevent gel formation by keeping the branches short.[71] An alternative route to the desired *cis*-1,4-polybutadiene microstructure is available via ring opening metathesis polymerisation of cyclobutene and this method gives more control over the molecular weight and also ensures that the desired product contains 100% 1,4-*cis* units.

2.1.2 DERIVATISATION OF POLYBUTADIENE

In polybutadiene the residual double bond in each monomer unit is either in the backbone or pendant from the polymer chain. The selective functionalisation of one or other of these double bonds is of great interest as it results in novel polymers with varying reactivities at different sites. For example, these double bonds may undergo epoxidation,[72], [73] hydroformylation,[74], [75] oxidation,[72] hydrocarboxylation [76], [77] and hydrosilation.[78], [72]

2.1.3 OXIDATION OF POLYBUTADIENE

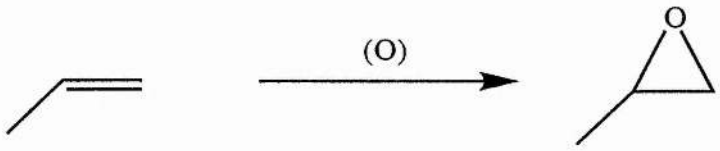
Polyketones can be prepared by the oxidation of polybutadiene with tert-butylhydroperoxide catalysed by [Pt(diphoe)(CF_3)(CH_2Cl_2)] BF_4 (diphoe = Z-Ph_2PCH=$CHPPh_2$).[72] This catalyst system gives high conversion of double bonds pendant from the backbone (i.e. terminal) to methyl ketones but only low conversions of the backbone double bonds to ketone units. It has recently been shown that polybutadiene containing pendant double bonds can be converted to polyketones using low oxygen pressure and catalytic amount of $PdCl_2$ and $CuCl_2$ in 1,2-dimethoxyethane.[68] An alternative route to the polyketone from *cis*-polybutadiene would involve epoxidation of the backbone double bonds followed by the isomerisation of epoxide groups to ketones.

2.1.4 EPOXIDATION OF POLYBUTADIENE

From the literature on epoxidation of polybutadienes as discussed earlier it was evident that most of the work previously carried out was concerned with stoichiometric reactions either with organic peroxides[79,80] or via catalytic reactions (involving Bu^tOOH and [MoO_2(acac)$_2$]),[81] all of which exhibited some selectivity for epoxidation. Recently, [MoO_2Cl_2L], L=[(1R)-endo]-(+)-3(diethoxyphosphoryl) camphor], a more active epoxidation catalyst than [MoO_2(acac)$_2$],[73] the structure of which is shown on page 48 has been developed. The diethoxyphosphoryl derivative of camphor has been shown to increase both the rate and the yield of the epoxidation reaction.

2.2 EPOXIDATION

Epoxidation (Equation 2.1) is an important reaction in organic synthesis because the formed epoxide is an important organic intermediates that can undergo ring-opening reactions to mono- or bi-functional organic products. Propene oxide is produced on large scale via the molybdenum catalysed epoxidation of propene.



Equation 2.1: General epoxidation reaction of a simple alkene.

In general, epoxides can be prepared by oxidation using alkylhydroperoxides in the presence of high-valent transition metal catalysts.

2.2.1 MOLYBDENUM EPOXIDATION CATALYSIS

Molybdenum complexes[82,83] are probably the best catalysts for epoxidation when using alkyl hydroperoxides as the oxidant. The most frequently used and tested monomeric molybdenum-ligand complexes are probably $[Mo(CO)_6]$ and $[MoO_2(acac)_2]$ as they achieve high yields when used to catalyse the epoxidation of alkenes. Most molybdenum complexes can successfully catalyse the epoxidation of alkenes although the yields of the epoxide are lower than those achieved with $[MoO_2(acac)_2]$.

The first step in the molybdenum catalysed epoxidation using $[MoO_2(acac)_2]$ with peroxides is the conversion of the peroxide to a peroxo-metal intermediate. The binding of the alkyl peroxide takes place through the terminal oxygen, but the other oxygen is also involved in coordination to the molybdenum, leading to a bidentate coordinated molybdenum alkyl peroxide complex. The coordination of the peroxide to the molybdenum leads to an activation of the peroxide to oxygen providing transfer to the alkene to form the epoxide.

The catalytic properties of the molybdenum complexes are, to a certain extent, dependent on the ligands attached to molybdenum. Since most suitable catalyst precursors are themselves octahedral, it is necessary for a ligand to dissociate to create a vacant site for co-ordination of the alkyl hydroperoxides. In a ß-ketophosphonate bidentate ligand developed by Gahagan et al[73], one of the donor atoms is only weakly bound to the molybdenum centre so that it stabilises the catalyst precursor but readily deco-ordinates to allow co-ordination of the tert-butylhydroperoxide (Bu^tOOH).

These ß-ketophosphonate complexes of molybdenum have been used in the epoxidation of simple alkene and larger molecules such as polybutadiene and have been shown to produce high yields with very few side reactions.[72,73]

2.2.2 [MoO_2Cl_2 (diethoxyphosphoryl) camphor] CATALYST AND IT'S USE IN THE EPOXIDATION OF POLYBUTADIENE

When polybutadienes containing both backbone and pendant double bonds are used as substrates, most epoxidation catalysts will either give incomplete conversion of the backbone double bonds or will exhibit conversion of pendant and terminal double bonds before the backbone has been completely converted.[80] A new catalyst, a complex of molybdenum dioxide dichloride and a camphor derived ß-diketophosphonate ligand (figure 2.5), recently developed by Gahagan et al[73] has been shown to be more selective to the epoxidation of backbone double bonds than the previous methods.

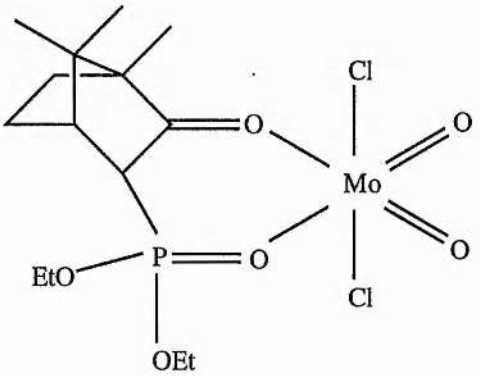


Figure 2.5: Dichloro(diethoxyphosphorylcamphor)dioxomolybdenum (VI) ([MoO_2Cl_2L], where L=(diethoxyphosphoryl)camphor.)

A comparison of [$MoO_2(acac)_2$] with [MoO_2Cl_2L] in the epoxidation of polybutadiene[72], containing 47% vinyl double bonds and 53% *cis*-1,4 and *trans*-1,4 double bonds, indicated that the [$MoO_2(acac)_2$] was not as active to epoxidation of the backbone double bonds as the [MoO_2Cl_2L] catalyst. For example, it was found that when using the [MoO_2Cl_2L] catalyst, the backbone double bonds were selectively epoxidised to a high extent (>95%) in less than three hours, in which time less than 50% of the backbone double bonds were epoxidised using the [$MoO_2(acac)_2$]. [$MoO_2(acac)_2$] showed preference for the backbone double bonds (*cis*-1,4 > *trans*-1,4 >> 1,2) but in no case has very high selectivity been observed; the terminal double bonds either start to epoxidise before the backbone double bonds, or some of the backbone double bonds remain unreacted. In contrast, the [MoO_2Cl_2L]

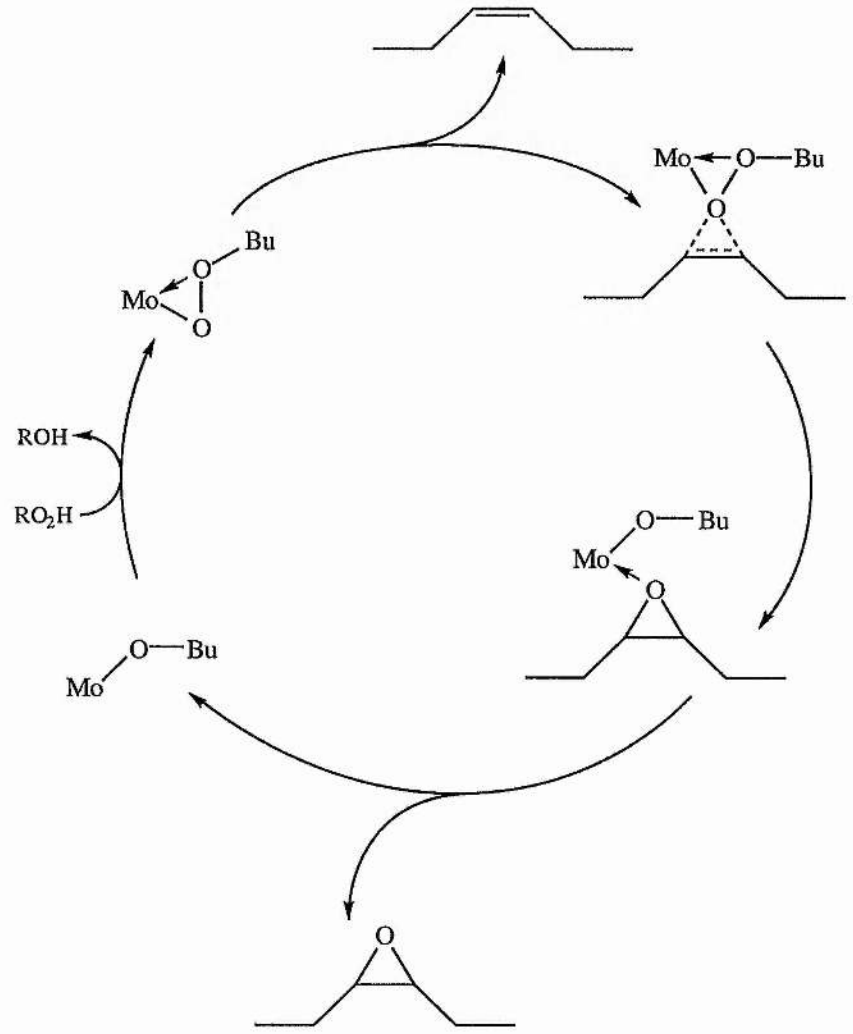
catalyst showed high selectivities for the epoxidation of the backbone double bonds in a variety of polymers and no conversion of pendant double bonds.

This catalytic enhancement observed with $[MoO_2Cl_2L]$ (figure 2.1) is thought to be due to the lability of the carbonyl oxygen atom of its bidentate ligand. This atom is weakly bound to the molybdenum centre, so that it stabilises the catalyst but readily decoordinates to allow co-ordination of the Bu^tOOH. Evidence also exists which indicates that $[MoO_2Cl_2L]$ catalyses the epoxidation of more electron-rich, internal and tri-substituted double bonds much faster than it does terminal double bonds.[72]

Although this catalyst eventually gives complete conversion of the backbone double bond in eighteen hours, experimental evidence indicates that adventitious water in the system causes ring-opening of some of the epoxides in which the resultant diols displace the diethoxyphosphoryl camphor ligand to form a less active catalyst. To alleviate this problem reactions were carried out in the presence of molecular sieves as it was shown previously by Clarke et al that the molecular sieves not only scavenge water but also bind the MoO_2 group with expulsion of the organic ligand.[84,85] In order to obtain highly epoxidised polymers which would be useful substrates for further functionalisation to a polyketone, *cis*-polybutadiene and *cis*-polyisoprene, the substrates of interest in this work were epoxidised with Bu^tOOH catalysed by $[MoO_2Cl_2L]$ in the presence of molecular sieves.

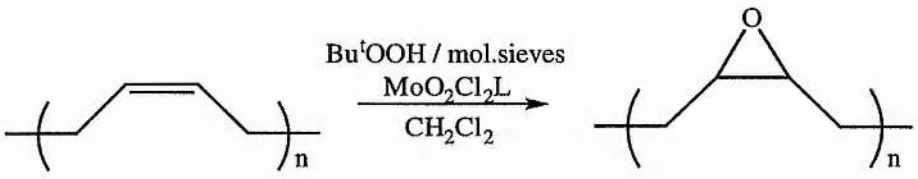
2.2.3 EPOXIDATION OF POLYBUTADIENE USING $[MoO_2Cl_2L]$

The work previously reported by A. Iraqi[72] concerning the epoxidation of polybutadiene using the $[MoO_2Cl_2L]$ catalyst indicated that this catalyst was effective for the epoxidation of internal double bonds. The Bartlett "Butterfly" mechanism (scheme 2.1) shows the nucleophilic attack of the alkene on the electrophilic oxygen of the coordinated hydroperoxide. It is thought that when the metal-hydroperoxide complex forms, the hydroperoxide is bound covalently to the metal through the oxygen atom distal to the alkyl group. The proximal oxygen atom is then thought to interact with the metal in the transition state further activating the hydroperoxide toward nucleophilic attack. (scheme 2.1)



Scheme 2.1: The mechanism for the molybdenum catalysed epoxidation of internal alkenes using tert-butylhydroperoxide.

When we applied this catalyst to the epoxidation by Bu^tOOH of a polybutadiene containing 99% *cis*-1,4 double bonds, molecular weight of 2-3,000,000, it was found that the backbone double bonds were epoxidised to a high extent to give a polyepoxide with the microstructure shown in the equation below.



Equation 2.2: Epoxidation of polybutadiene with Bu^tOOH catalysed by MoO_2Cl_2L in the presence of molecular sieves.

Conversions to epoxide greater than 95% were observed, as can be seen from the ^1H NMR - spectrum 2.1 shown on page 53. The extent of epoxidation was determined quantitatively by integration of resonance at 5.45 ppm (unreacted double bonds), 3.0 ppm (epoxide groups) and at 4.0 ppm (diol groups). In addition the ^1H NMR shows the hydrogens of the methylene groups as a multiplet at 1.7 ppm due to the different environments of the methylene groups brought about by the orientation of the epoxide.

Confirmation that the complete conversion of the backbone double bonds had occurred was provided by the lack of a resonance at 130 ppm and the presence of two characteristic resonances for the epoxide at 56.6 and 56.9 ppm in the ^{13}C NMR, see spectrum 2.2 page 54. The methylene groups between each epoxide are observed in the ^{13}C NMR at 25.1 and 25.3 ppm along with excess Bu^tOOH (80.8 ppm) and the resultant Bu^tOH (69 ppm). Other resonances observed are from isooctane, the solvent of the Bu^tOOH.

The two characteristic resonances observed for the epoxide are due to the structural orientation of the epoxide groups as indicated by figure 2.6 below. A detailed analysis of the NMR spectra of the epoxides is given in section 2.2.6, page 62.

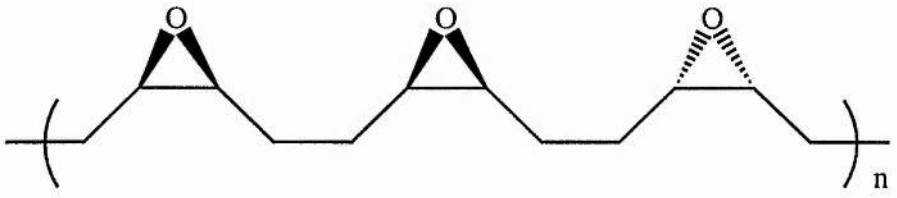


Figure 2.6: Structural orientation of polybutadiene epoxide.

The infra red spectrum which shows characteristic bands for the epoxide at 905 and 965 cm^{-1}, as shown by spectrum 2.3 on page 55, supports the information obtained from NMR analysis. Other characteristic stretches for the catalyst ligand,

diethoxyphosphorylcamphor, are also observed at [ν(C=O] at 1742 and [ν(P=O)] at 1250 cm^{-1} [86] along with general stretching and bending modes of a hydrocarbon polymer.

2.2.4 EFFECT OF MOLECULAR SIEVES ON EPOXIDE FORMATION

Molecular sieves have previously been used to scavenge adventitious water in the epoxidation of simple alkenes using the $[MoO_2Cl_2L]$ catalyst. A number of observations reported indicated that the role of the molecular sieves[84] is not simply to scavenge water but rather that both the catalyst and the Bu^tOOH binds to the molecular sieves which greatly increases the reaction rate and yield, even with styrene which is generally difficult to epoxidise in high yield and selectivity.

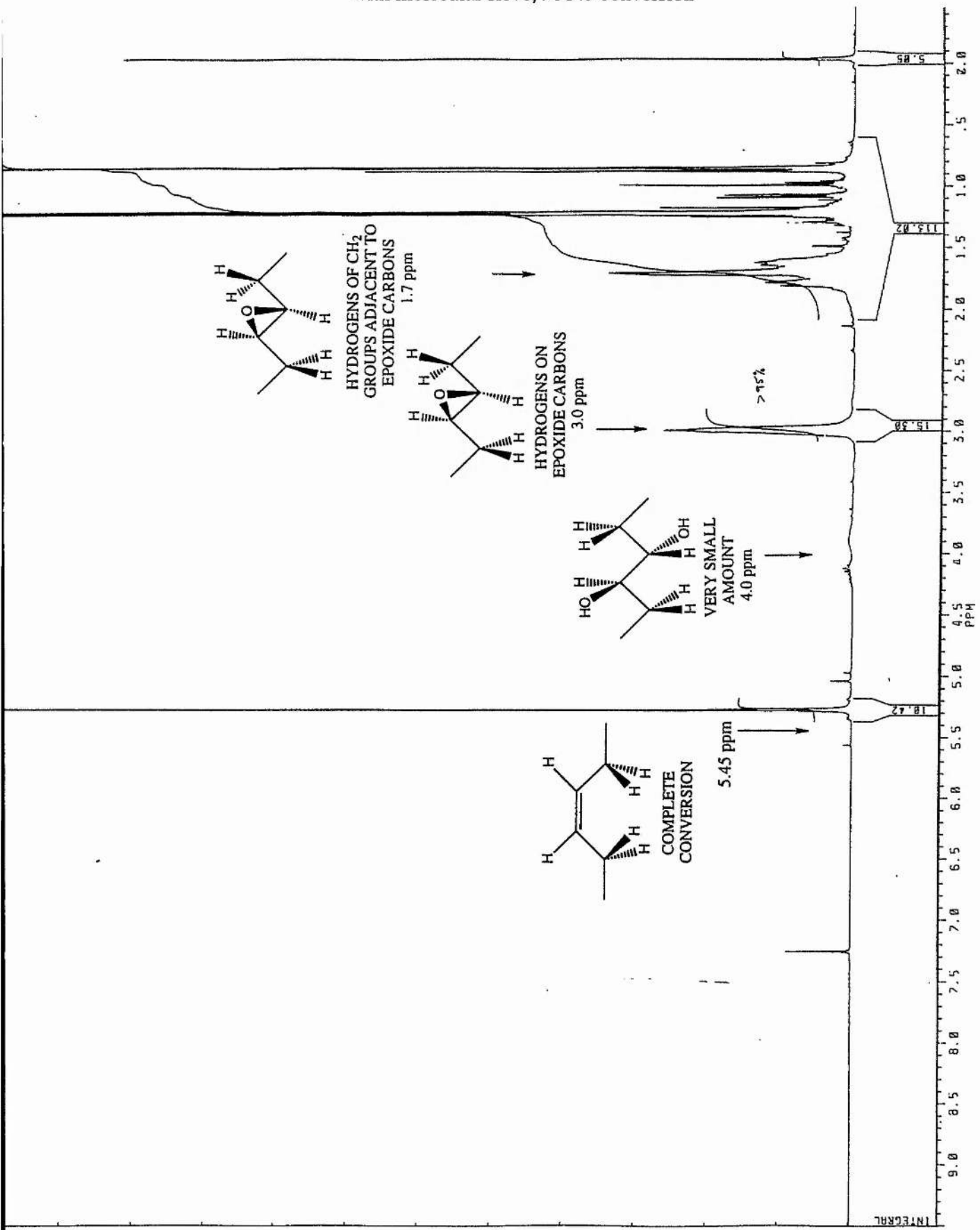
Difficult separation of the high molecular weight polymer (2-3,000,000) from molecular sieves led to the investigation of epoxidation reactions without molecular sieves and reactions with different molecular weight polybutadiene. Hence, the percentage conversion to the epoxide for reactions with and without molecular sieves were compared as shown in table 2.1 on page 57, using integrations calculated from ^1H NMR spectra. These results indicated that reactions carried out in the presence of molecular sieves gave higher conversions to the epoxide than those without. It has been previously suggested[84] that the initial highly active catalyst is replaced by a less active form, perhaps by the reaction of water in the system.

Moreover, reactions involving the epoxidation of the 99% *cis*-1,4-polybutadiene gave important information regarding the catalyst. An absorption at 1695 cm^{-1} was observed in samples of polyepoxide produced from the epoxidation of *cis*-1,4-polybutadiene using $[MoO_2Cl_2L]$ in the absence of molecular sieves showing that intact catalyst is still present, but when the reaction was carried out in the presence of molecular sieves, no absorption of the free catalyst was observed but only an absorption at 1742 cm^{-1} corresponding to ϑ (C=O) for the free ß-ketophosphonate ligand. These observations confirm that the ligand is lost from the molybdenum centre in reactions involving molecular sieves and are consistent with the molybdenum binding to the molecular sieves, spectrum 2.4 page 56.

Spectrum 2.1

Polyepoxide (HMWT-PBD) - ^{1}H NMR

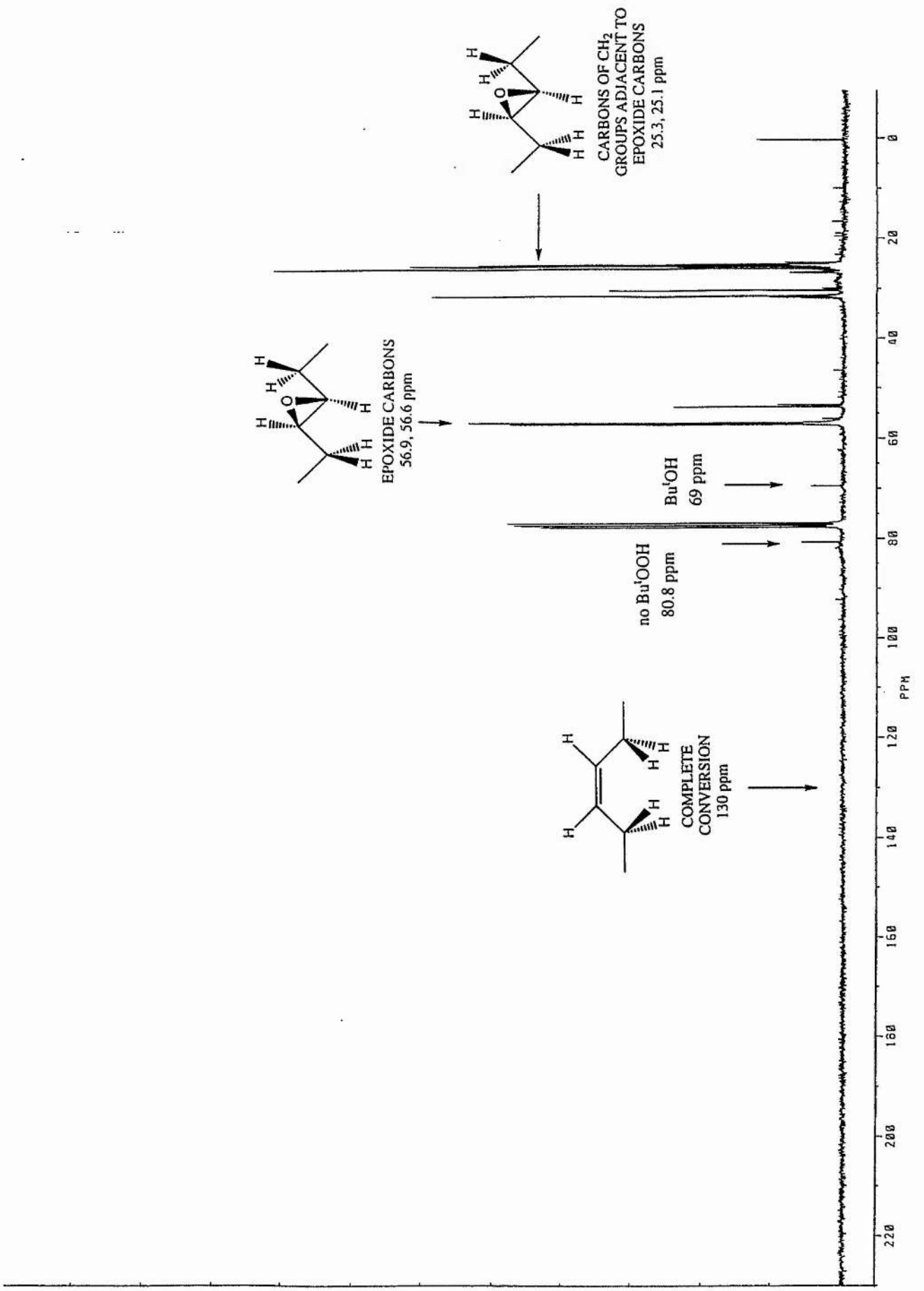
with molecular sieve, >95% conversion



Spectrum 2.2

Polyepoxide (HMWT-PBD) - ^{13}C NMR

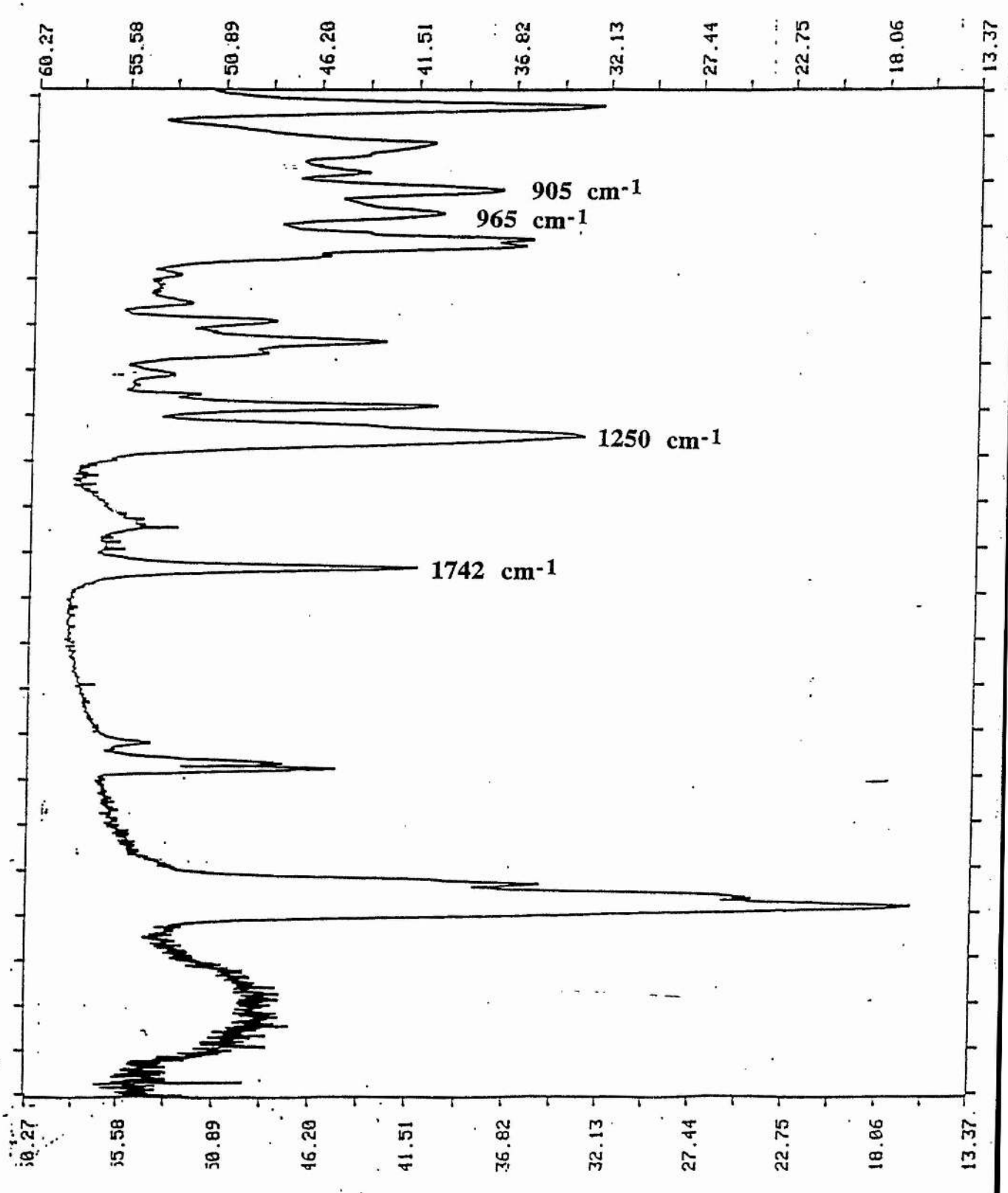
with molecular sieves



Spectrum 2.3

Polyepoxide (HMWT-PBD) - FTIR

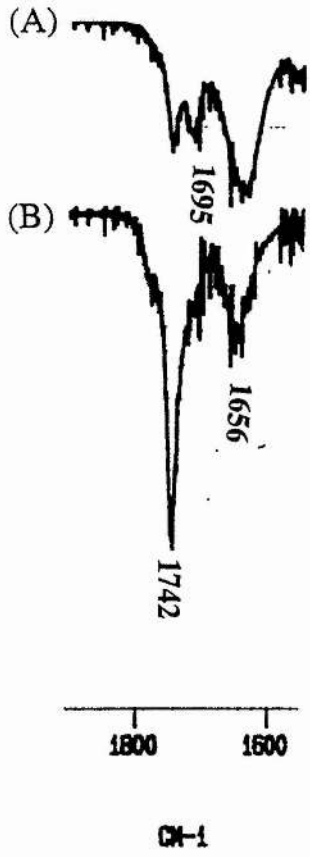
with molecular sieves



Spectrum 2.4

Polybutadiene epoxide - FTIR

without (A) and with (B) molecular sieves



The nature of the active catalyst was subsequently investigated by low temperature NMR, see page 88.

The results in table 2.1 (page 57) indicate that the use of molecular sieves and their subsequent removal from the polymer solution are necessary in order to attain a highly epoxidised polymer. The removal of the molecular sieves is achieved by introducing a lower molecular weight polybutadiene, its low viscosity in solution allows the molecular sieve to settle to the bottom of the flask and then the polymer solution can be decanted off. Initially, the LMWT polybutadiene used had a *cis/trans*/vinyl microstructure as this was readily available, which was later replaced by a LMWT *cis*-polybutadiene which has a more suitable mircostructure in relation to the polyketone desired.

TABLE 2.1

CONVERSION TO EPOXIDE OF HIGH MOL WT *cis* (A)

AND LMWT *cis/trans*/vinyl POLYBUTADIENE (B)

REACTION	MOLECULAR SIEVES	% CONVERSION		% UNREACTED DOUBLE BONDS *cis/trans*
		EPOXIDE *cis/trans*	DIOL *	
A RUN 1	√	90	NONE	NONE
A RUN 2	√	66	2	31
A RUN 3	√	86	5	8
A RUN 4	-	45	NONE	55
A RUN 5	-	30	70	NONE
A RUN 6	-	60	NONE	40
B RUN 1	-	90/ 70	6	6/ 26
B RUN 2	-	85/ 95	10	7/ 2
B RUN 3	-	80/ 80	40	NONE

A - Polybutadiene with 99% *cis* double bonds (M.W.= 2-3,000,000).

B - Polybutadiene with 40% *cis*, 40% *trans* and 20% pendant double bonds (Mn = 5,000).

* - From these results it was noted that reactions which involved the interaction molecular sieves gave higher percentage conversions to the epoxide and less diol formation than those without molecular sieves. The diol [72] (microstructure shown below) is formed due to the ring opening of the epoxide by adventitious water in the system.

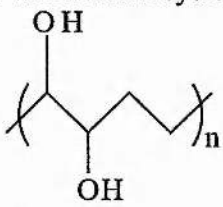


Figure 2.7: Ring opened polybutadiene epoxide by adventitious water

2.2.5 EPOXIDATION REACTIONS OF LOW MOLECULAR WEIGHT POLYBUTADIENE

cis-1,4-Polybutadiene with a molecular weight of 2-300,000 was epoxidised using $[MoO_2Cl_2L]$ in the presence and absence of molecular sieves. The results are collected in table 2.2. Using the lower molecular weight polybutadiene, it proved straight forward to remove the molecular sieves either by allowing them to settle over one week or by centrifugation followed by filtration.

TABLE 2.2

CONVERSION TO EPOXIDE OF LOW MOL WT POLYBUTADIENE (PBL)

REACTION	MOLECULAR SIEVES	% CONVERSION		% UNREACTED DOUBLE BONDS *cis/trans*
		EPOXIDE *cis*	DIOL *	
RUN 1	√	>95	NONE	NONE
RUN 2	√	>95	NONE	NONE
RUN 3	√	>95	NONE	NONE
RUN 4	√	>95	NONE	NONE
RUN 5	√	>95	NONE	NONE
RUN 6	√	>95	NONE	NONE
RUN 7	√	>95	NONE	NONE
RUN 8[a]	-	82	18	NONE
RUN 9[a]	-	77	23	NONE
RUN 10[a]	-	60	30	NONE
RUN 11[a]	-	87	13	NONE

PBL - Polybutadiene with 99% *cis* double bonds (M.W.= 2-300,000)

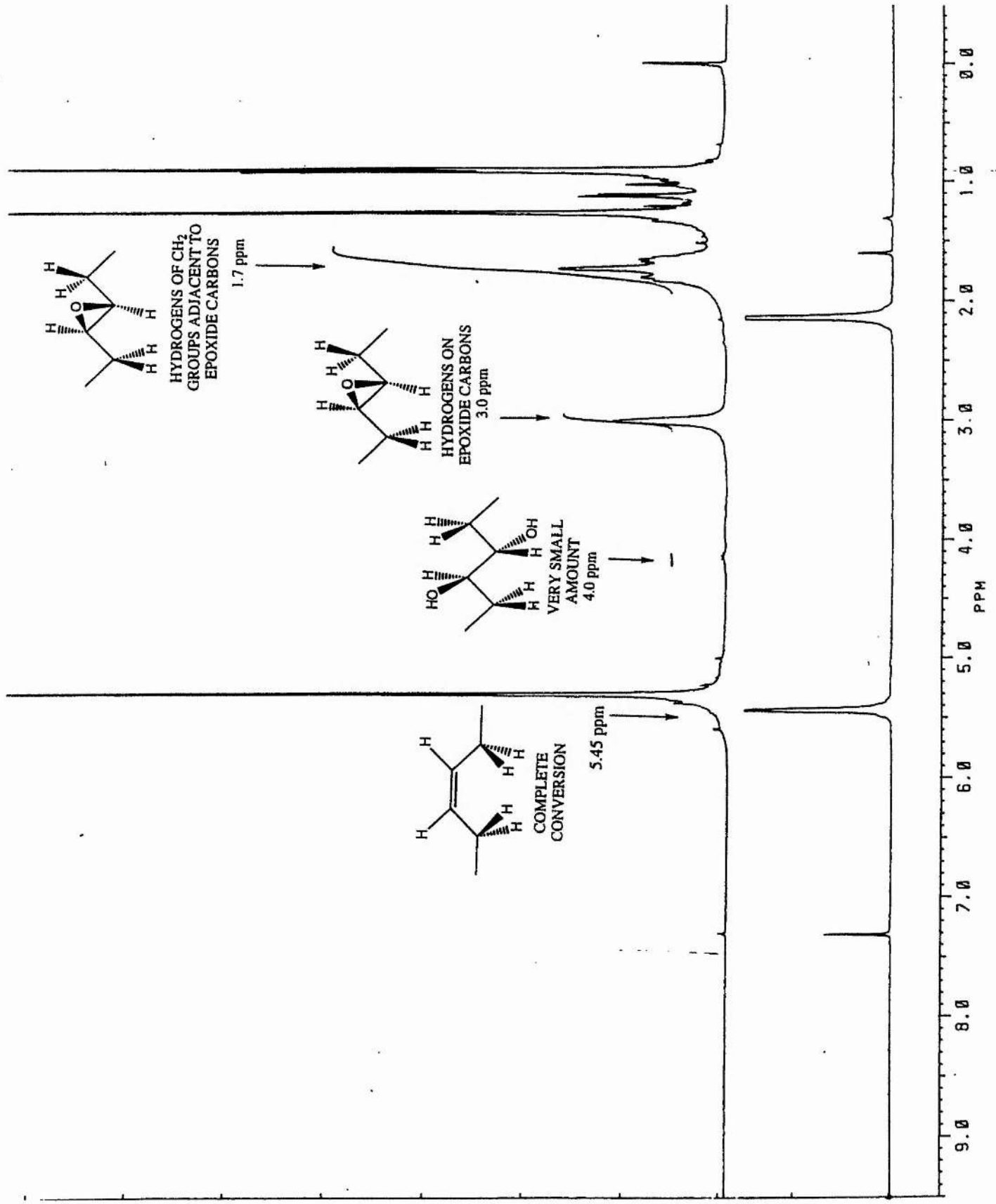
a - Excess catalyst, double that generally used.

* - Diol - see structure on previous page.

Typically, ^1H NMR analysis shows the high conversion to the epoxide from a study of the relative integrations of the epoxide (3.0 ppm), diol (4.0 ppm) and unreacted double bond resonances (5.45 ppm), which is supported by the lack of characteristic methylene peaks for the polybutadiene (2.15 ppm) and the presence of characteristic methylene peaks for the epoxide (1.7 ppm), spectra 2.5 on page 59.

Spectra 2.5

Polybutadiene and polybutadiene epoxide - ^1H NMR
with molecular sieves



The ^{13}C NMR not only confirms this high conversion to the epoxide by the lack of characteristic double bond resonances at 130 ppm, but also shows two resonances for the epoxide carbons at 56.6 and 56.9 ppm and two for the methylene groups of the epoxidised polymer at 25.1 and 25.3 ppm. In addition, the DEPT NMR confirms these assignments and distinguishes between the epoxide carbons (CH) and the methylene carbons (CH_2), spectra 2.6 on page 61.

Impurities from the solvent CH_2Cl_2, Bu^tOH from the oxidant Bu^tOOH and the iso-octane solvent from the oxidant are evident in both spectra. The DEPT NMR also enables the determination of the peaks at 54.0 ppm for CH_2 group of the dichloromethane, 69.0 ppm for the tertiary carbon ($\mathbf{C}(CH_3)_3$) of the Bu^tOH, 32.0 ppm for the CH_3 groups of the Bu^tOH. In addition, the CH, CH_2 and CH_3 groups of iso-octane, the solvent in which the Bu^tOOH is supplied, show characteristic peaks at 24.9, 25.5, 31.0 and 53.8 ppm.

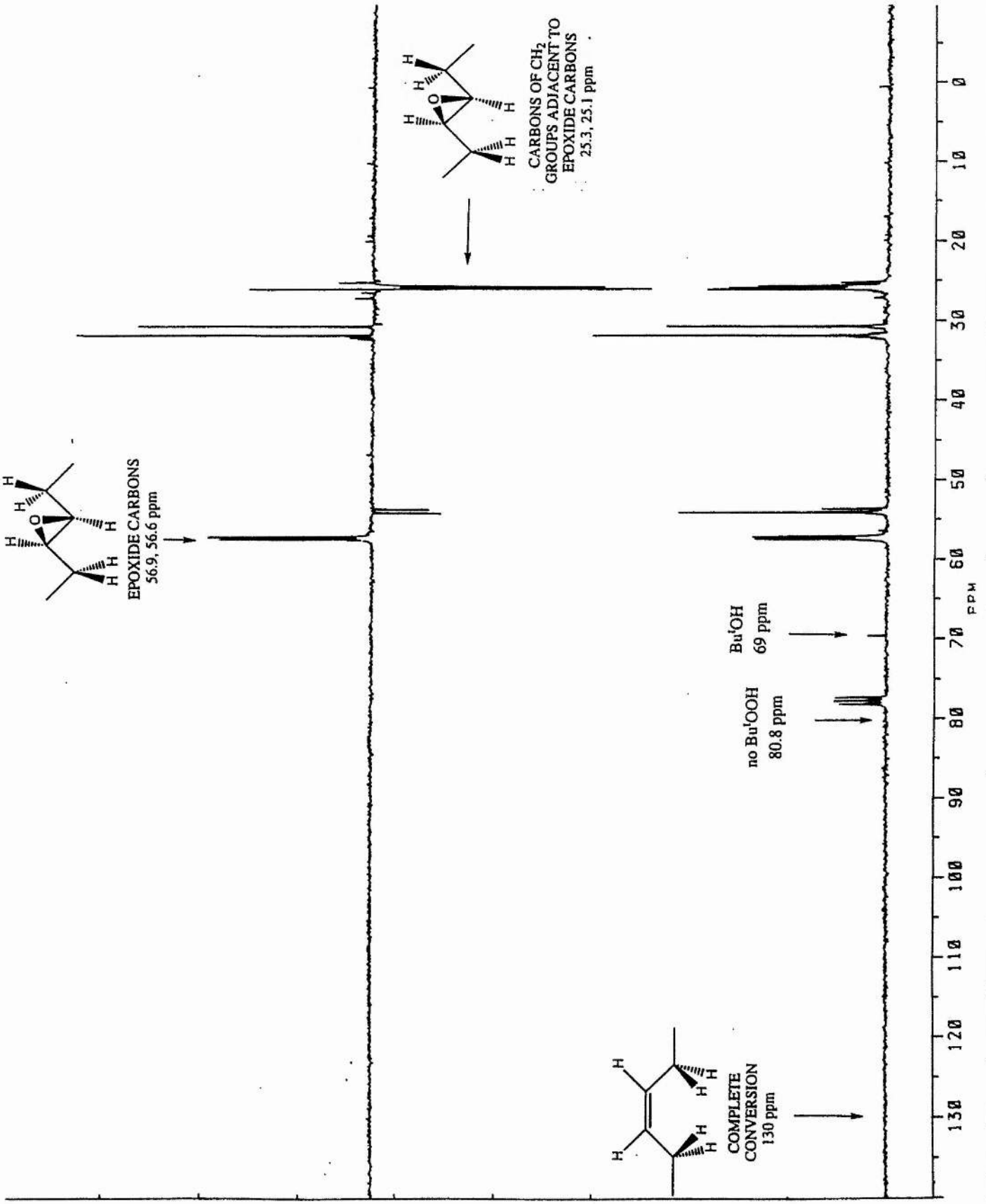
Complete conversion of the backbone double bonds was shown by the lack of a characteristic double bond resonance at 5.45 ppm in the ^1H NMR and at 130 ppm in the ^{13}C NMR. In addition, greater than 95% selectivity was suggested by the lack of characteristic double bond resonances and the absence of characteristic diol resonances at 4.0 ppm in the ^1H NMR and 82 ppm in the ^{13}C NMR and supported by the absence of characteristic Bu^tOOH peaks in the ^1H and ^{13}C NMR, when the oxidant is used in stoichiometric amounts.

Purification of these polymers proved difficult, as many attempts to remove the impurities resulted in an insoluble product. After precipitation with petrol the polymer could not be re-dissolved in any solvent. This indicates the possibility of crosslinking, an understanding of which led to the successful purification of the polyepoxide and will be discussed in more detail later (see pages 75-6).

Spectra 2.6

Polybutadiene epoxide - ^{13}C and DEPT NMR

with molecular sieves



2.2.6 SPECTROSCOPIC PROPERTIES OF THE POLYBUTADIENE EPOXIDE

The ^{1}H and ^{13}C NMR spectra of the polyepoxides produced in the presence of molecular sieves show that only resonances characteristic of the polyepoxide are present, with no evidence for unreacted double bonds or diol formation. Of particular interest is the observation that the ^{13}C resonance of the epoxide carbon atoms in the polyepoxide appears as two peaks of equal intensity at 56.6 and 56.9 ppm. We assign these as arising from the random orientation of the epoxide oxygen atoms at either side of the chain. For the polybutadiene epoxide, one resonance arises from carbon atoms (carbon 1 in the diagram below) for which the oxygen atom of the next epoxide is on the same side of the chain as that in the epoxide of the carbon atoms in question (X), whilst the second resonance is from carbon atoms (carbon 2 in the diagram, unit Y) where the next oxygen atom is on the opposite side of the chain (units Y and Z below).

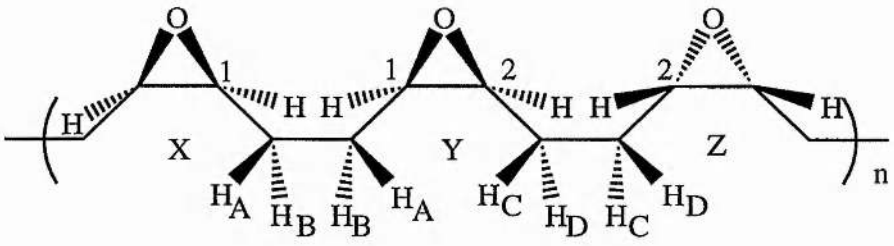


Figure 2.8: Structural orientation of the epoxide groups and the methylene groups in polybutadiene epoxide.

This random orientation also gives rise to non-equivalences in the CH_2 protons of the chain, which resonate as a broad triplet in the ^{1}H NMR. Examination of the structure of the polymer in its least sterically hindered conformation (figure 2.9) shows that the H atoms of each methylene unit are inequivalent but the H atoms of pairs of methylene groups are related by a local centre of inversion (CH_AH_B) or a local 2 fold axis perpendicular to the plane of the polymer backbone (CH_CH_D) (assuming that the environment of the H atoms is only affected by the epoxide groups on each side of the methylene group in question).

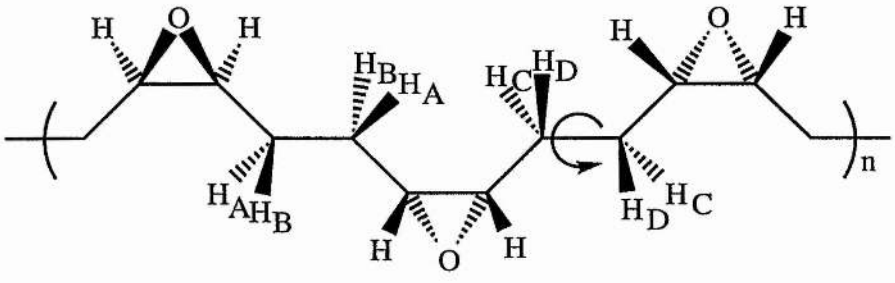


Figure 2.9: Structure of polybutadiene epoxide in its least sterically hindered conformation

It seems probable then that the higher field signal of the broad triplet is from H_D (on the opposite side of the chain from both adjacent epoxide atoms) and the lower field signal is from H_C (on the same side as both adjacent O atoms). The resonances from H_A and H_B then overlap since they have an adjacent oxygen atom on the same side of the chain and the other on the opposite side. Therefore, explaining the broad triplet observed centred at 1.7 ppm in the ^1H NMR in which the intensity is 1:2:1.

2.2.7 CONCLUSIONS FOR EPOXIDATION OF POLYBUTADIENE

The epoxidation of polybutadiene can be effectively carried out with Bu^tOOH catalysed by $[MoO_2Cl_2L]$ in the presence of molecular sieves which can be then easily removed when the molecular weight of the polymer is low. Complete conversion of the backbone double bonds is evident and high selectivity to the epoxide is confirmed by the absence of diol resonances. The detailed spectroscopic study indicates that the orientation of the epoxide group in the polymer affects the chemical shift of the adjacent C and H atoms and that the epoxide oxygen atoms are randomly oriented on either side of the polymer chain.

Although complete conversion of the backbone double bonds is achieved with high conversion to the epoxide using this method, problems with purification of the polymer needed to be resolved. Essentially, the polymer when precipitated from the dichloromethane solution would not re-dissolve due to crosslinking. This problem has been solved and will be discussed at the end of this chapter.

2.3. EPOXIDATION OF POLYISOPRENE

2.3.1 SYNTHESIS OF POLYISOPRENES

The polymerisation of isoprene may be accomplished by a variety of methods.[87] The choice of method has a profound effect on the microstructure of the resulting polymer, figures 2.10-2.13.

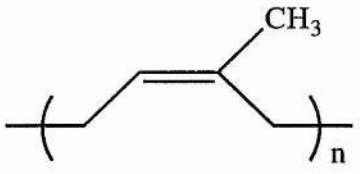


Figure 2.10: cis-1,4-polyisoprene

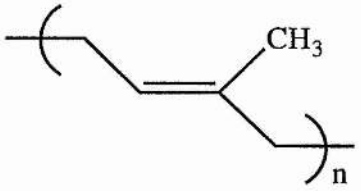


Figure 2.11: trans-1,4-polyisoprene

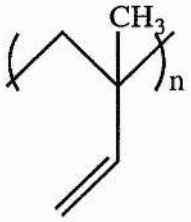


Figure 2.12: 1,2-polyisoprene

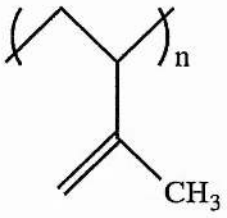


Figure 2.13: 3,4-polyisoprene

The only polyisoprenes which have acceptable properties and which are of commercial importance are those of a high *cis*-1,4 content (although a small amount of high *trans*-1,4-polyisoprene is produced as a replacement for gutta percha).

Three catalyst systems have been used for the production of *cis*-1,4-polyisoprene, namely coordination catalysts (e.g. titanium tetrachloride-tri-isobutylaluminium), lithium and alkyl lithium compounds (e.g. butyl lithium). The microstructures produced with these catalysts are very similar as shown in the table 2.3 on the next page.

TABLE 2.3

EFFECT OF INITIATOR ON THE MICROSTRUCTURE OF POLYISOPRENE

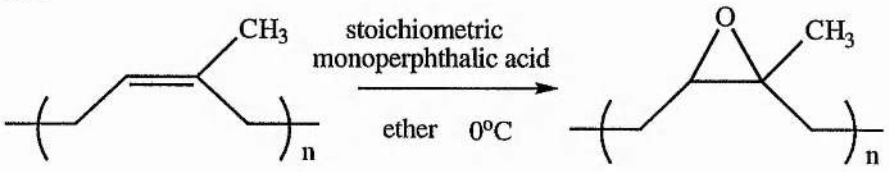
	% STRUCTURAL UNITS			
INITIATOR	*cis*-1,4	*trans*-1,4	1,2-	3,4-
Free Radical	22	65	6	7
Li	94	0	0	6
Li n-Bu	93	0	0	7
α-$TiCl_3$-$AlEt_3$	96	0	0	4

The 1,4-polyisoprene can also be prepared via a free radical polymerisation although this results in a mixture of the *cis* and *trans* isomer, in which the *trans* isomer predominates as it is thermodynamically favoured especially at low temperatures.

2.3.2 DERIVATISATION OF POLYISOPRENE

Polyisoprene like polybutadiene has double bonds in the polymer which are available for functionalisation. These double bonds can be either in the backbone or pendant in each monomer unit as shown in the figures 2.10-2.13.

cis-1,4-polyisoprene is almost indistinguishable from natural rubber which can be cyclised, hydrohalogenated or halogenated to give other polymers. It has been shown that polyisoprene can be epoxidised using monoperphthalic acid[88] in stoichiometric amounts, see equation below.



Equation 2.3: Epoxidation of polyisoprene with monoperphthalic acid.

2.3.3 EPOXIDATION OF POLYISOPRENE USING $[MoO_2Cl_2L]$ IN THF

Epoxidation reactions of polyisoprene using $[MoO_2Cl_2L]$ were carried out in a similar fashion to those of polybutadiene, except that the solvent used was tetrahydrofuran (THF) as it dissolved the polyisoprene more readily than any other solvent. Initially, the percentage conversion to epoxide and/or diol could not be determined because characteristic peaks for the diol at ~4.0 ppm in the ^1H NMR were masked by those of the THF, spectrum 2.7 on page 67. Without knowing the amount of diol produced it was difficult to assess the amount of epoxide present, although characteristic epoxide resonances were observed at ~60 ppm and ~64 ppm in the ^{13}C NMR spectra, see table 2.4. In most cases the ^{13}C NMR (spectrum 2.8, page 68)

showed no characteristic diol resonance at 82 ppm indicating that no diol was formed. If diol units were present, resonances should be observed near 82 ppm, as in the spectrum of the polybutadiene epoxide obtained from the oxidation in the absence of molecular sieves (spectrum 2.9, page 69).

TABLE 2.4

EPOXIDATION OF POLYISOPRENE (PI) IN THF

		CONVERSION				UNREACTED DOUBLE BONDS *cis*
		EPOXIDE - *cis*		DIOL		
REACTION[a]	SOLVENT	^{1}H NMR / ^{13}C NMR		^{1}H NMR / ^{13}C NMR		
RUN 1	THF	2.9	60 + 64	not observed due to THF	not observed at 82	NONE
RUN 2	THF	2.9	60 + 64	not observed due to THF	not observed at 82	NONE
RUN 3	THF	2.9	60 + 64	not observed due to THF	not observed at 82	NONE
RUN 4	THF	2.9	60 + 64	not observed due to THF	not observed at 82	NONE
RUN 5	THF	2.9	60 + 64	not observed due to THF	not observed at 82	NONE
RUN 6	THF	2.9	60 + 64	not observed due to THF	not observed at 82	NONE
RUN 7	THF	2.9	60 + 64	not observed due to THF	not observed at 82	NONE

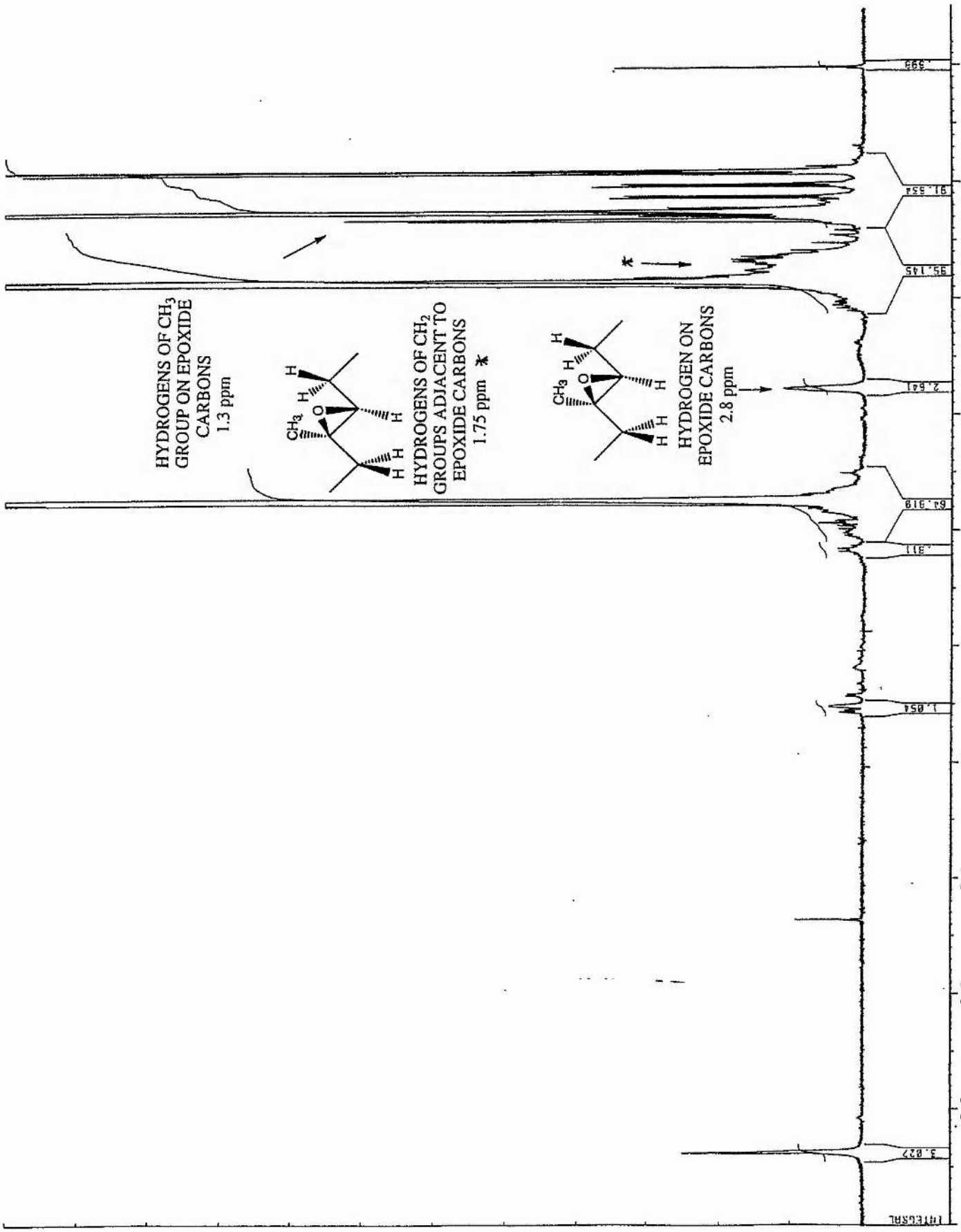
PI - Starting material was polyisoprene with 99% *cis double* bonds
(M.W.= 2-300,000)
a - All reactions were carried out in the presence of molecular sieves.

Complete conversion of the backbone double bonds in the polyisoprene was confirmed from the NMR spectra in which the characteristic double bond resonances at 5.6 ppm in the ^{1}H NMR and at 125 and 135 ppm in the ^{13}C NMR were absent. (see spectra 7 and 8). Also observed in the ^{13}C NMR of the polyisoprene epoxide was the presence of resonances at 100 and 107 ppm which will be discussed in Chapter 3 page 118.

Spectrum 2.7

Polyepoxide (LMWT-PISOP) - ^{1}H NMR

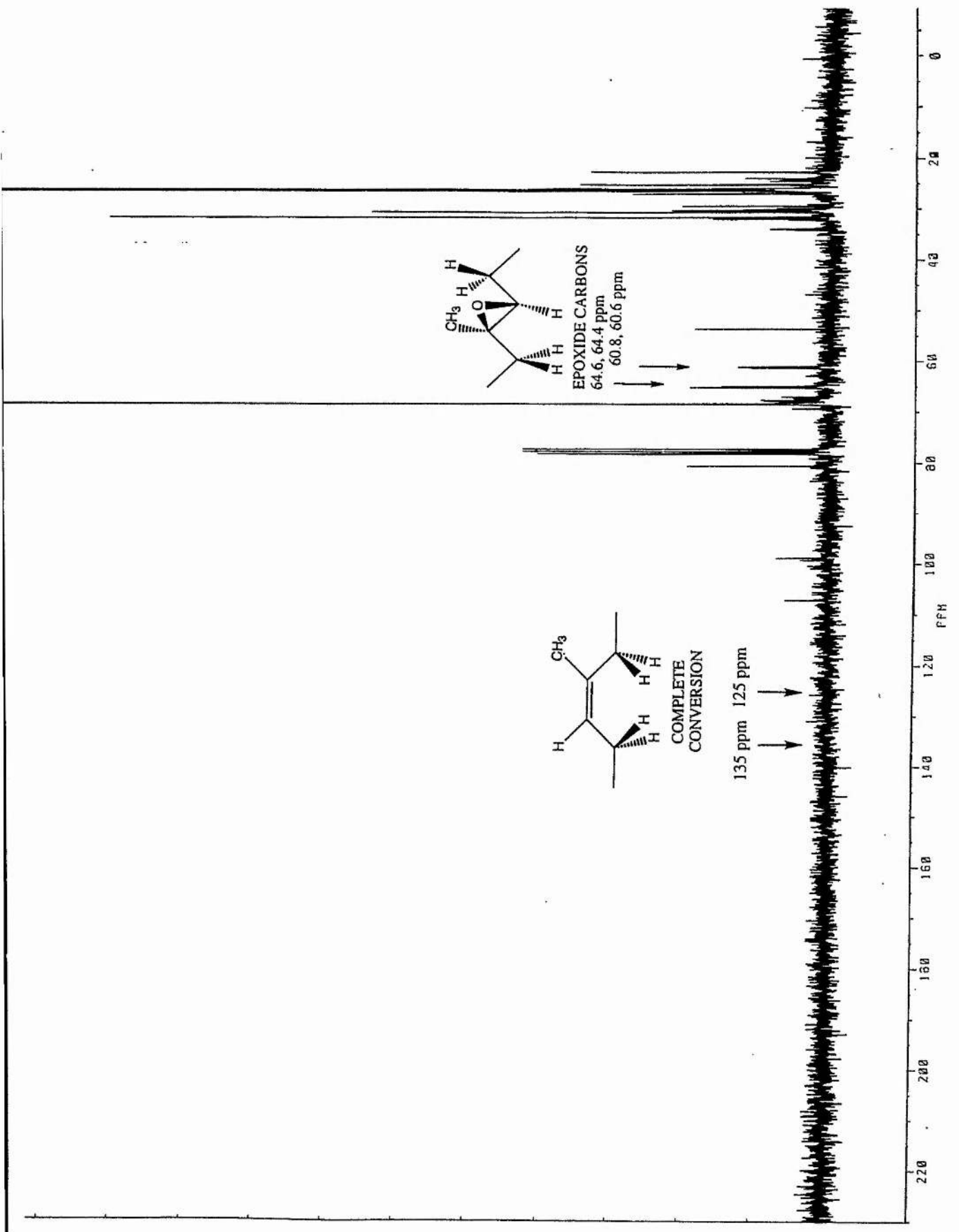
with molecular sieves in THF



Spectrum 2.8

Polyepoxide (LMWT-PISOP) - ^{13}C NMR

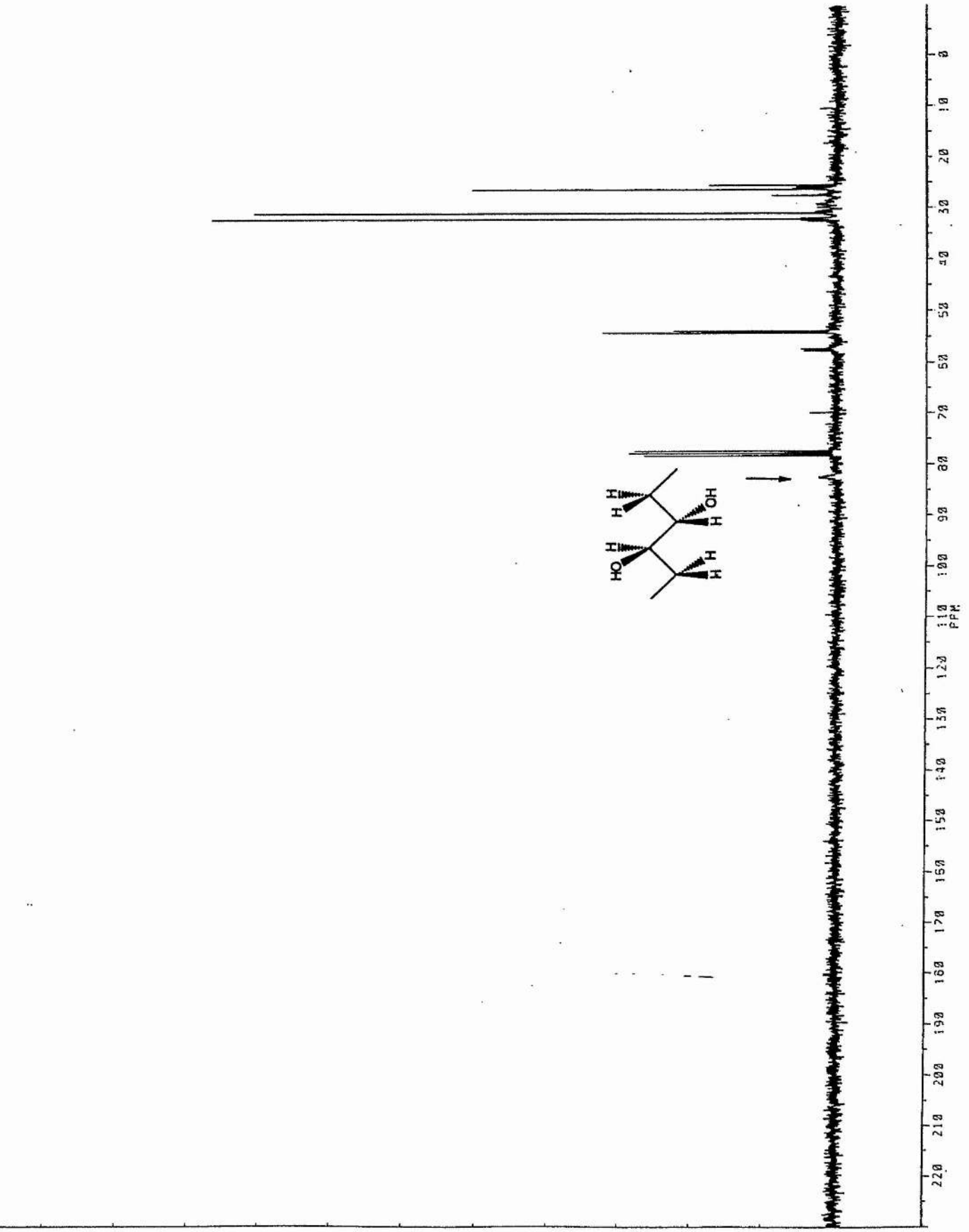
with molecular sieves in THF



Spectrum 2.9

Polyepoxide (LMWT-PBD) - ^{13}C NMR

without molecular sieves in CH_2Cl_2



2.3.4 QUANTITATIVE EPOXIDE CONVERSION OF POLYISOPRENE

Because of the problems encountered with quantitative analysis of the product in reactions carried out in THF, epoxidation of polyisoprene in CH_2Cl_2, was used to determine the epoxide / diol conversions. Tables 2.4 (page 66) and 2.5 (below) show the results for the epoxidation of the polyisoprene in both solvents and in each case molecular sieves were used to remove adventitious water from the system preventing the deactivation of the molybdenum catalyst.

TABLE 2.5

CONVERSION OF POLYISOPRENE (PI) TO EPOXIDE IN CH_2Cl_2

REACTION[a]	SOLVENT	% CONVERSION		% UNREACTED DOUBLE BONDS
		EPOXIDE	DIOL	
RUN 8	CH_2Cl_2	>95	NONE	NONE
RUN 9	CH_2Cl_2	>95	NONE	NONE
RUN 10	CH_2Cl_2	>95	NONE	NONE
RUN 11	CH_2Cl_2	>95	NONE	NONE

PI - Starting material was polyisoprene with 99% *cis* double bonds
(M.W.= 2-300,000)
a - All reaction were carried out in the presence of molecular sieves.

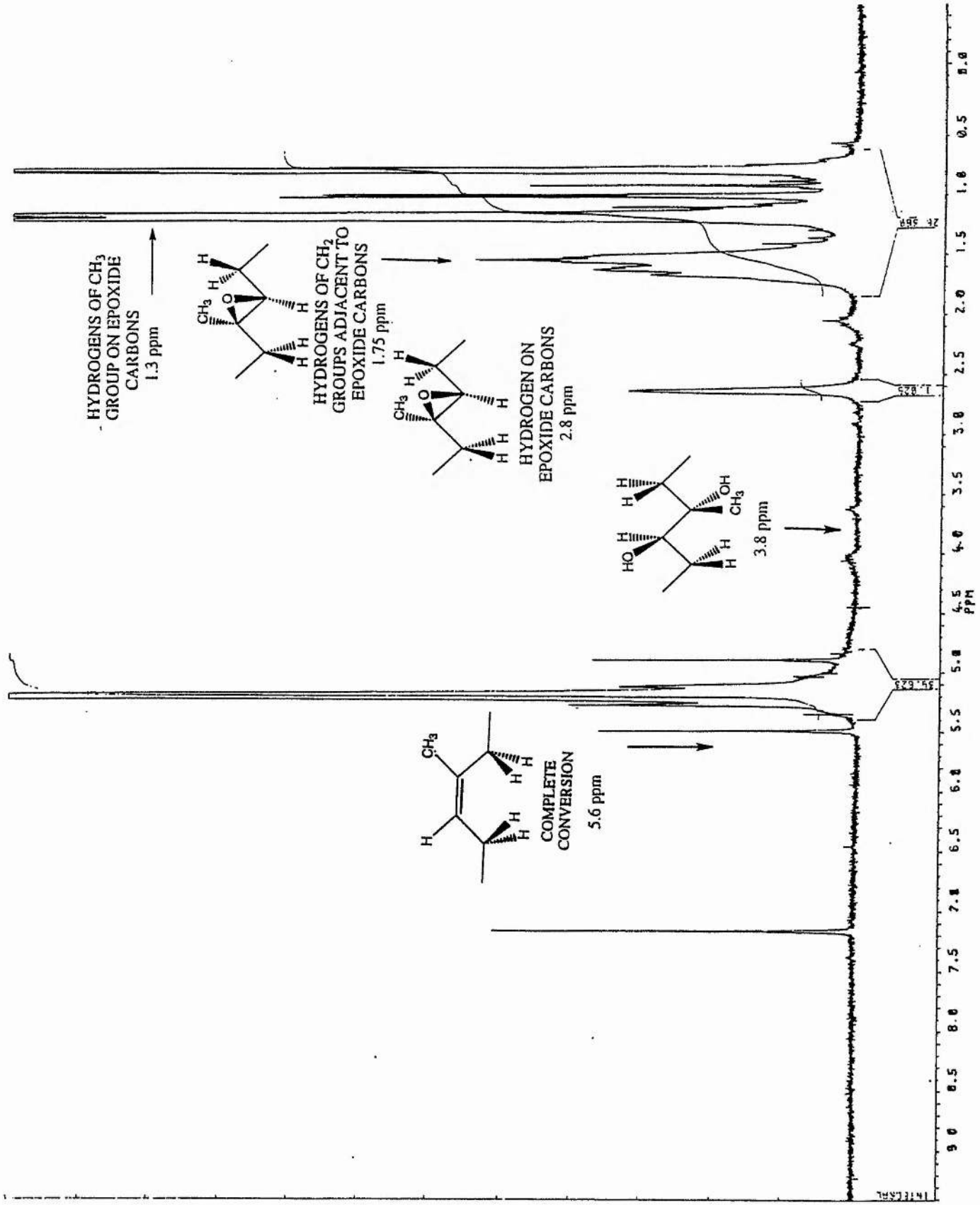
Epoxidation of low molecular weight *cis*-polyisoprene using Bu^tOOH catalysed by $[MoO_2Cl_2L]$, in the presence of molecular sieves gives high conversions to the epoxide with little or no diol being formed. As indicated by reactions carried out in dichloromethane polyisoprene is as easily converted to the epoxide as polybutadiene although the time to dissolve the polyisoprene in dichloromethane is longer. Nevertheless the end result is the same, complete conversion of the backbone double bonds and greater than 95% selectivity to the epoxide, spectra 2.10 and 2.11 on page 71 and 72.

The purification of the polyisoprene epoxide showed the same problems as the polybutadiene epoxide. The polymer, when precipitated with petrol to remove free ligand, Bu^tOOH and iso-octane, would not re-dissolve due to crosslinking. A method of purification which avoids crosslinking is discussed later, see page 75.

Epoxidation of polyisoprene with and without molecular sieves was also investigated and it was again found that the conversion to epoxide was much better when molecular sieves were used as indicated by the results in table 2.6 on page 73.

Spectrum 2.10

Polyepoxide (LMWT-PISOP) - ^1H NMR
with molecular sieves in CH_2Cl_2



Spectrum 2.11

Polyepoxide (LMWT-PISOP) - ^{13}C NMR
with molecular sieves in CH_2Cl_2

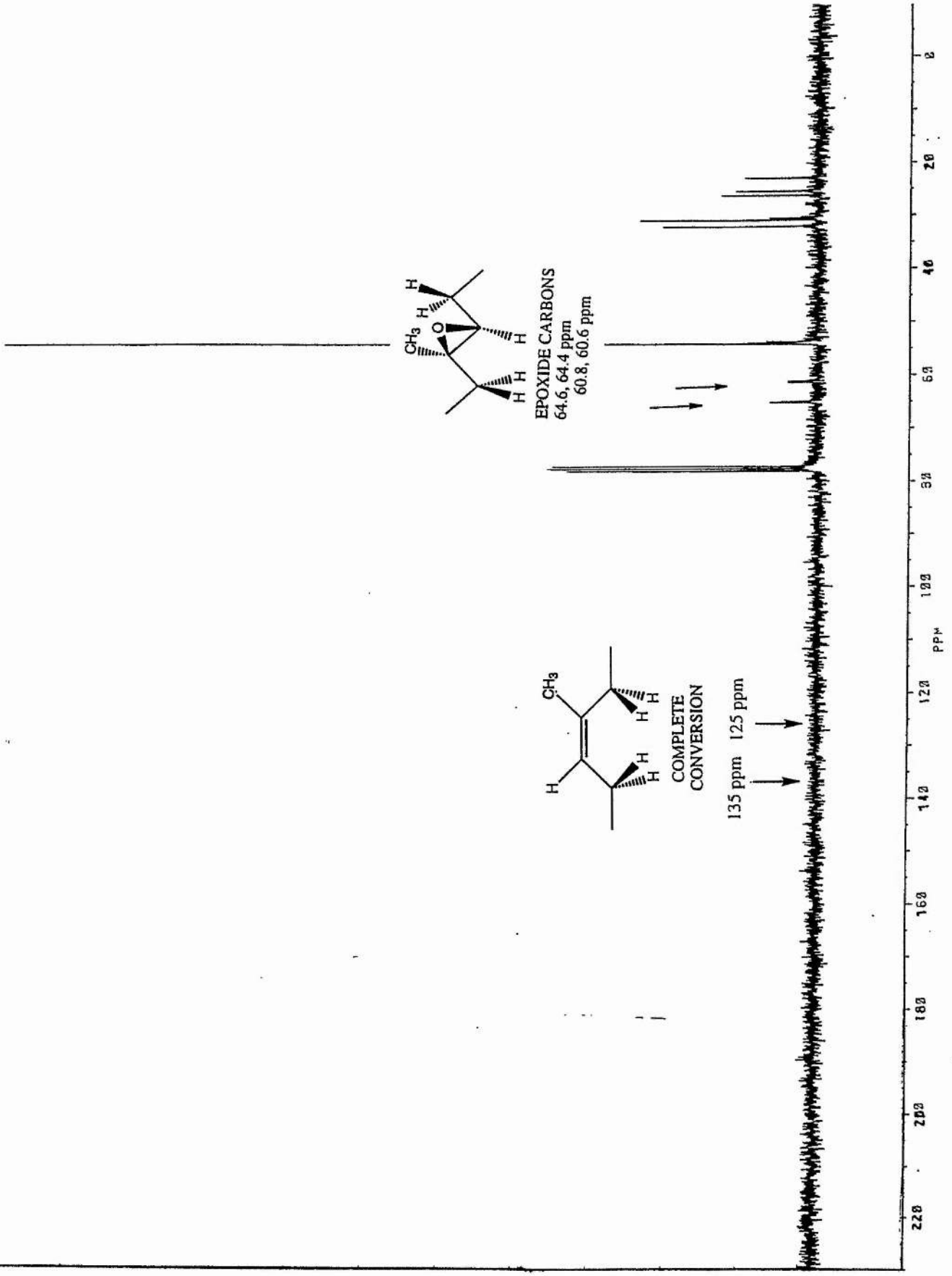


TABLE 2.6

CONVERSION OF POLYISOPRENE TO EPOXIDE IN CH_2Cl_2 WITH AND WITHOUT MOLECULAR SIEVES

REACTION	SOLVENT	MOL SIEVES	% CONVERSION		% UNREACTED DOUBLE BONDS
			EPOXIDE	DIOL	
PI 12	CH_2Cl_2	√	>95	NONE	NONE
PI 13	CH_2Cl_2	√	>95	NONE	NONE
PI 14	CH_2Cl_2	-	65	35	NONE
PI 15	CH_2Cl_2	-	70	30	NONE

PI - Starting material was polyisoprene with 99% *cis* double bonds (M.W.= 2-300,000)

The addition of the molecular sieves to the polyisoprene reactions has the same effect as with the epoxidation of polybutadiene. As discussed earlier the molecular sieves not only scavenge water but also allow the Mo catalyst and the Bu^tOOH to bind to them which increases the rate and yield of the reaction.[84]

In addition the molecular sieves also improve the purity of the polymer solution, as the molybdenum which is bound to the sieves may be easily removed by decanting and centrifuging the polymer solution to remove the sieves.

2.3.5 SPECTROSCOPIC STUDY OF POLYISOPRENE EPOXIDE

^1H and ^{13}C NMR analysis of the polymers formed in CH_2Cl_2 show that the only polymer resonances present are characteristic of the polyepoxide, with no evidence for unreacted double bonds or diol formation. Of particular interest is the observation that the ^{13}C resonance of each non-equivalent epoxide carbon atom in the polyisoprene appears as two peaks of equal intensity arising from the random orientation of the epoxide oxygen atoms at either side of the chain. For the epoxidised polyisoprene, the two carbon atoms of the double bond are not equivalent and give rise to resonances near 60.6, 60.8, 64.4 and 64.6 ppm, with both appearing as double peaks because of the random orientation of the epoxide linkages along the chain. One resonance at 60 ppm is due to the epoxide carbons attached to a proton for which the oxygen atom for the next epoxide carbon is on the same side of the chain as the carbon atom in question (**A** in figure 2.14), whilst the second resonance is from carbon atoms where the next oxygen is on the opposite side of the chain (**B** in figure 2.14). This is also the case for resonances at 64 ppm in which the epoxide carbons are attached to methyl groups (**C** and **D** in figure 2.14).

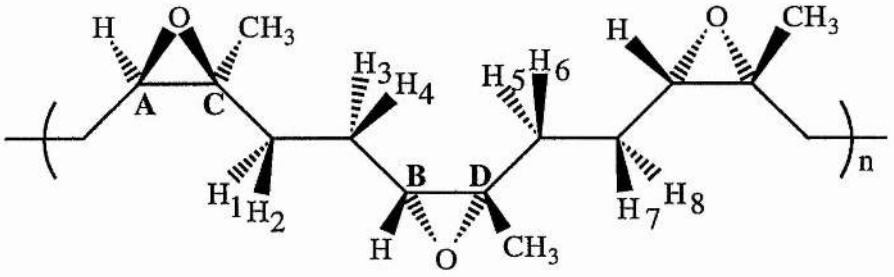


Figure 2.14: Structural orientation of polyisoprene epoxide in its least sterically hindered conformation showing four different epoxide carbon environments.

This random orientation ensures that there are eight different H environments for the methylene protons, but these appear as a broad series of lines (4 major ones but possible some weaker ones as well) near 1.75 ppm in the ^{1}H NMR. The epoxide protons resonate as a singlet despite the fact that the oxygen of the next epoxide in the chain can be on the same side or the opposite side of the chain relative to this proton. This suggests that the chemical shift of this proton is insensitive to the stereochemistry of the carbon atom delta to it.

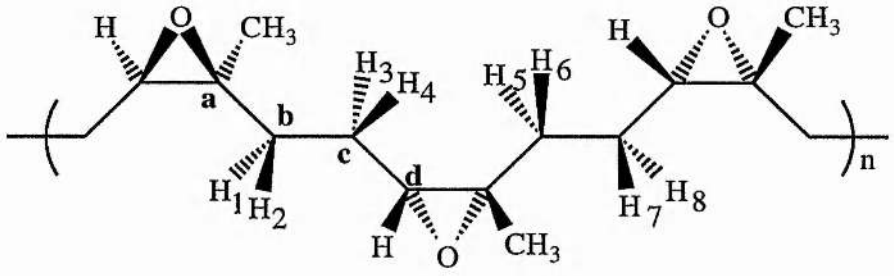


Figure 2.15: Structure of polyisoprene epoxide in its least sterically hindered conformation showing eight different proton environments.

Similarly, the methyl resonances of the isoprene units appear as a singlet at 1.35 ppm indicating that the stereochemistry of the methyl group on the epoxide is insensitive to the methyl group on the next epoxide carbon no matter if it is on the same side or opposite side of the chain. The methyl resonance in the ^{13}C NMR is observed at 23 ppm.

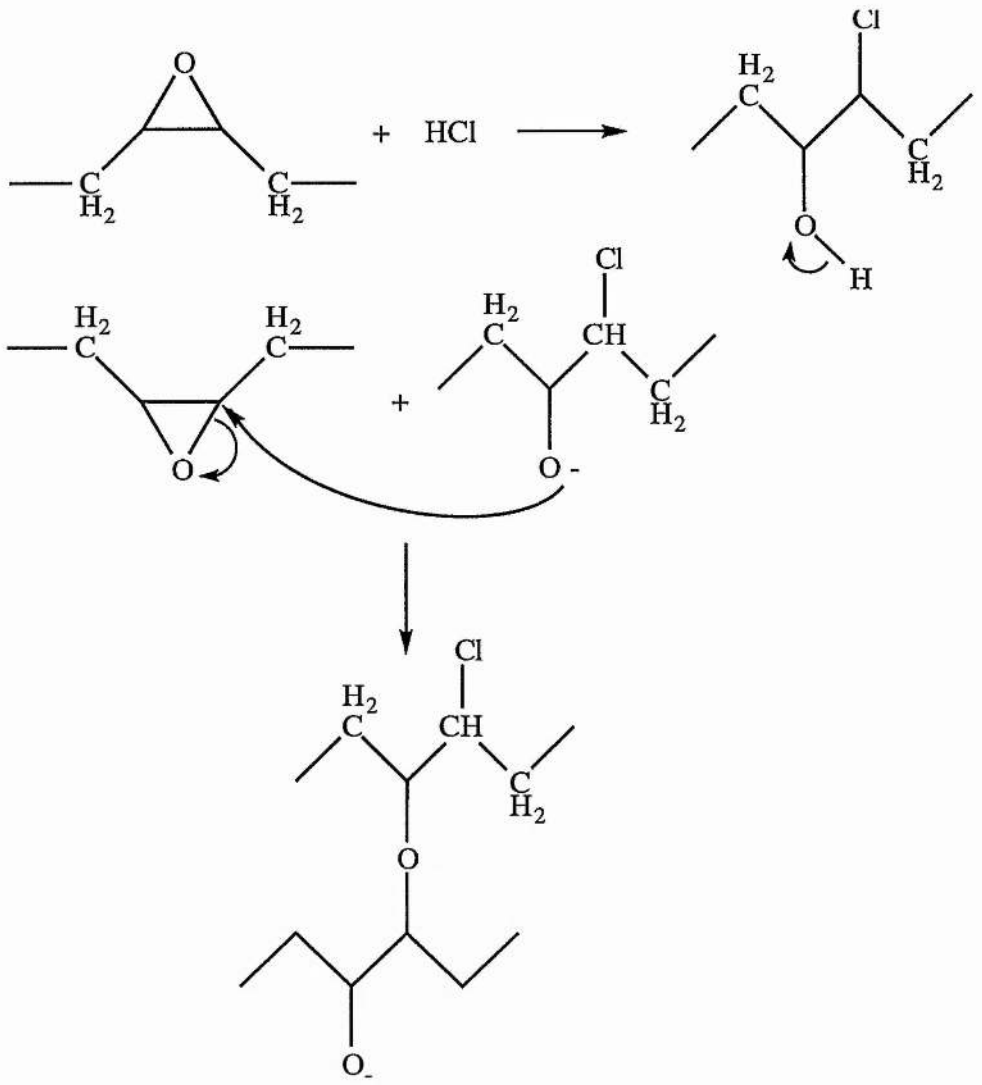
Two resonances for methylene groups between the epoxide carbons are observed at 25 and 30 ppm. Examination of the polyisoprene epoxide chain shows that there are two different methylene environments. One methylene carbon atom is directly attached to epoxide carbons with a methyl group. The other methylene carbon atom is directly attached to epoxide carbons with a hydrogen group.

2.4 PURIFICATION OF THE POLYEPOXIDE OF POLYBUTADIENE AND POLYISOPRENE

The polyepoxides obtained from polybutadiene and polyisoprene can be successfully purified so that the polyepoxide when precipitated may re-dissolve in dichloromethane or tetrahydrofuran respectively. Stoichiometric amounts of the oxidant are used and assuming the polydiene is completely converted to the epoxide no residual Bu^tOOH should be present. The lack of residual Bu^tOOH would also confirm the effectiveness of the catalyst in converting the backbone double bonds of the polymer, which is proven by ^{13}C NMR.

The crude polyepoxide solution consist of polymer, molecular sieves, diethoxyphosphorylcamphor and possibly some intact catalyst, Bu^tOH and HCl (from the $[MoO_2Cl_2L]$ catalyst). Initially, the majority of the molecular sieves is removed by leaving the polymer and molecular sieves to stand, to allow the molecular sieves to settle to the bottom of the flask so that the polymer solution can be easily removed. The polymer solution is then centrifuged to remove residual molecular sieves. These steps not only eliminate molecular sieves but also remove the MoO_2 which is bound to the molecular sieve leaving the ligand in solution.

Before the polymer is precipitated using petrol it is treated with calcium carbonate to remove hydrogen chloride produced by the catalyst during the process. The calcium carbonate reacts with the hydrogen chloride to give calcium chloride, carbon dioxide and water. The polymer solution is therefore centrifuged to remove the calcium chloride and any residual calcium carbonate. The hydrogen chloride produced by the catalyst is believed to be the source of the crosslinking when the polymer is precipitated as indicated by the proposed mechanism on the next page.



Scheme 2.2: Acid catalysed crosslinking within the polyepoxide.

This is supported when the hydrogen chloride free polymer is precipitated in petrol and then easily re-dissolved in dichloromethane or tetrahydrofuran several times to remove the remaining impurities. After the polymer is precipitated it is necessary for the polymer to be collected using a centrifuge, as the polymer is so fine that removal via filtration is difficult.

These purification procedures have allowed easy re-dissolution of the polymer which was previously insoluble after polymer precipitation.

2.4.1 SPECTROSCOPIC ANALYSIS OF THE PURIFIED POLYMERS

Analysis of the purified polymers by NMR indicated that no impurities remained. The only signals observed in the ^{13}C NMR are those of the epoxide carbons and those of the methylene groups situated between them and a trace of solvent as shown by the ^{1}H and ^{13}C NMR of the unpurified polybutadiene and polyisoprene epoxide, spectra 2.5, 2.6, 2.10, 2.11 on pages 59, 61, 71 and 72 compared to the purified polybutadiene and polyisoprene epoxide, spectra 2.12, 2.13, 2.14 and 2.15 on pages 78-81. Other signals observed are for the Bu^tOH or Bu^tOOH. This is confirmed by FTIR and in addition indicates that there is no intact catalyst and free ligand present in the polymer, spectrum 2.16 on page 82.

Atomic absorption analysis has shown that they contain appreciable amounts of molybdenum, up to 75% of the molybdenum from the catalyst used can remain in the polymer. Due to the amount of molybdenum in the polymer a slightly different epoxidation reaction was investigated, in which the molybdenum was bound to the molecular sieves and filtered prior to the addition of the substrate and the oxidant. The free ligand and residual Mo catalyst were removed via catheter leaving only the molybdenum that is retained within the molecular sieves, so that the molybdenum-molecular sieves can be easily removed leaving a pure polymer.

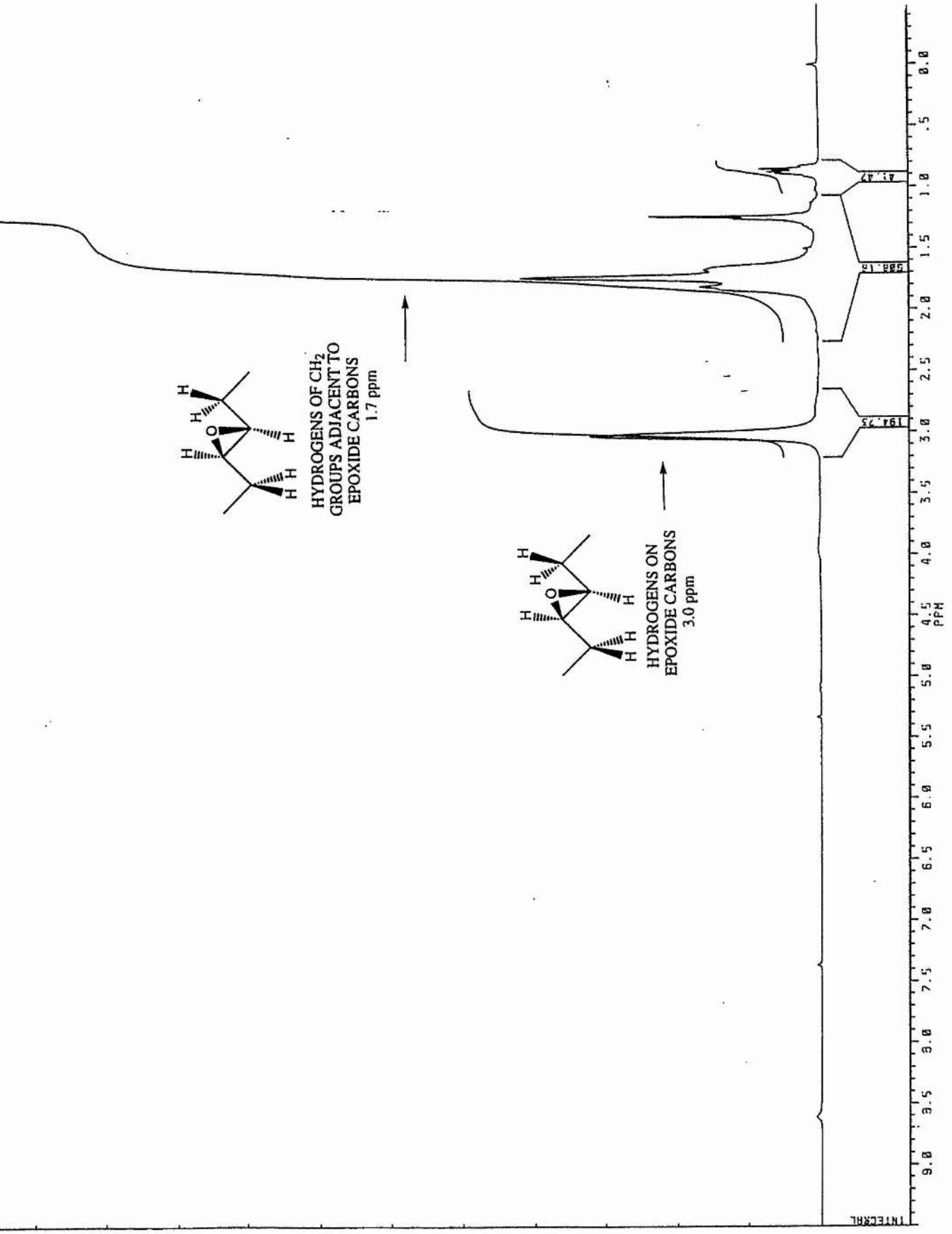
2.4.2 AN ALTERNATIVE EPOXIDATION REACTION TO IMPROVE PURIFICATION

Initially, a MoO_2/molecular sieves catalyst was prepared by adding $[MoO_2Cl_2L]$ to the molecular sieve in a dichloromethane solution. The MoO_2 group binds to the molecular sieves[84] leaving the free ligand and residual intact catalyst in the solution which is removed as mentioned above leaving only the MoO_2/molecular sieve. The substrate and the oxidant were then added and analysis by NMR indicated that the percentage conversion to the epoxide was just as high for the MoO_2/molecular sieves catalyst complex as it was for $[MoO_2Cl_2L]$. The ^{1}H NMR spectrum 2.17 the of polybutadiene epoxide is shown on page 83.

In addition, atomic absorption has shown that the level of molybdenum in the polyisoprene epoxide sample obtained via this reaction method is greatly reduced from 72.5% (found in a previous polyepoxide sample using the other epoxidation reaction) to 20%. This is also the case for the polybutadiene as the level of molybdenum is reduced from 14.7 to 12.1%, although this reduction is not as significant as for the polyisoprene, however the level within the polybutadiene is already low.

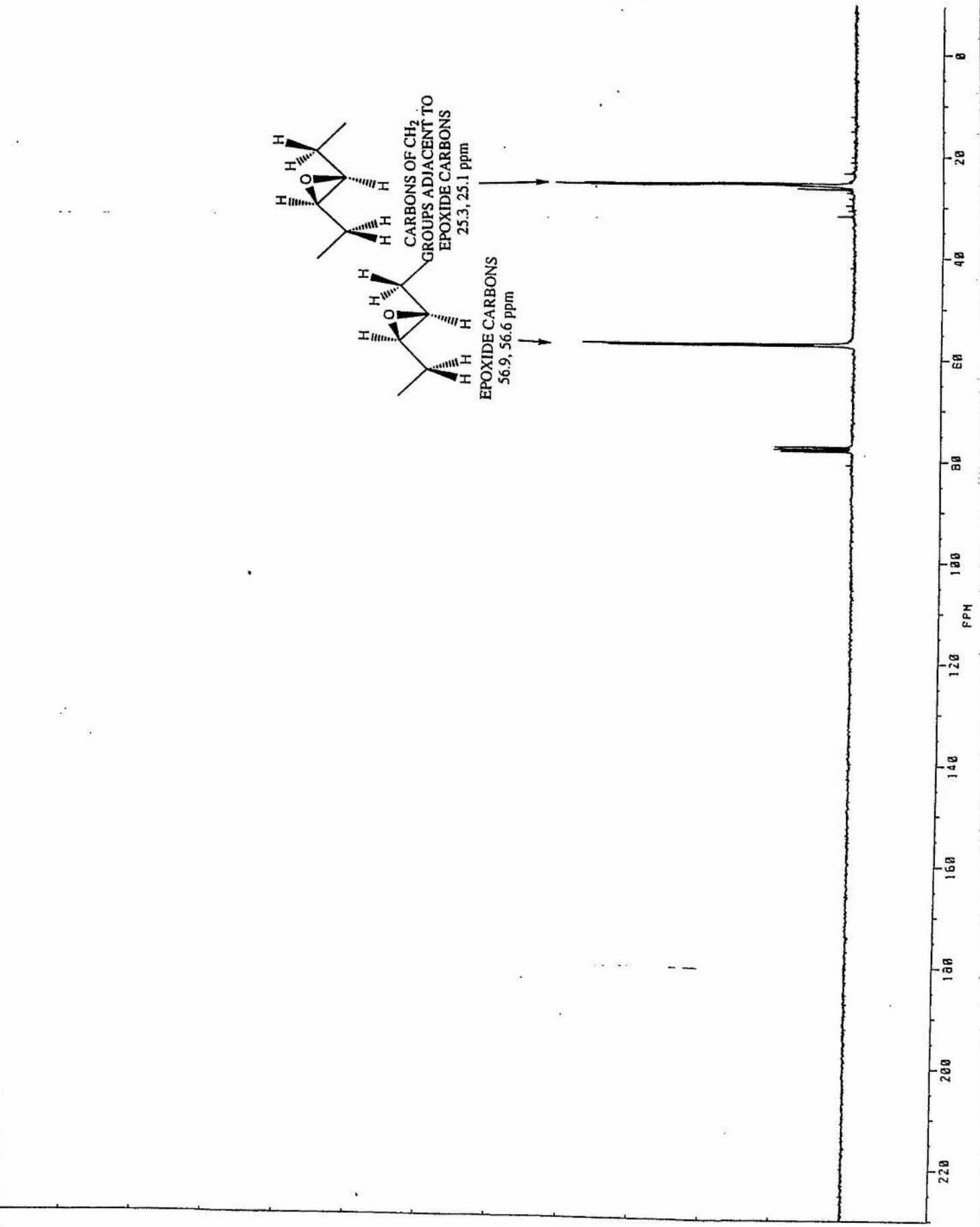
Spectrum 2.12

Purified Polyepoxide (LMWT-PBD) - ^1H NMR
with molecular sieves in CH_2Cl_2



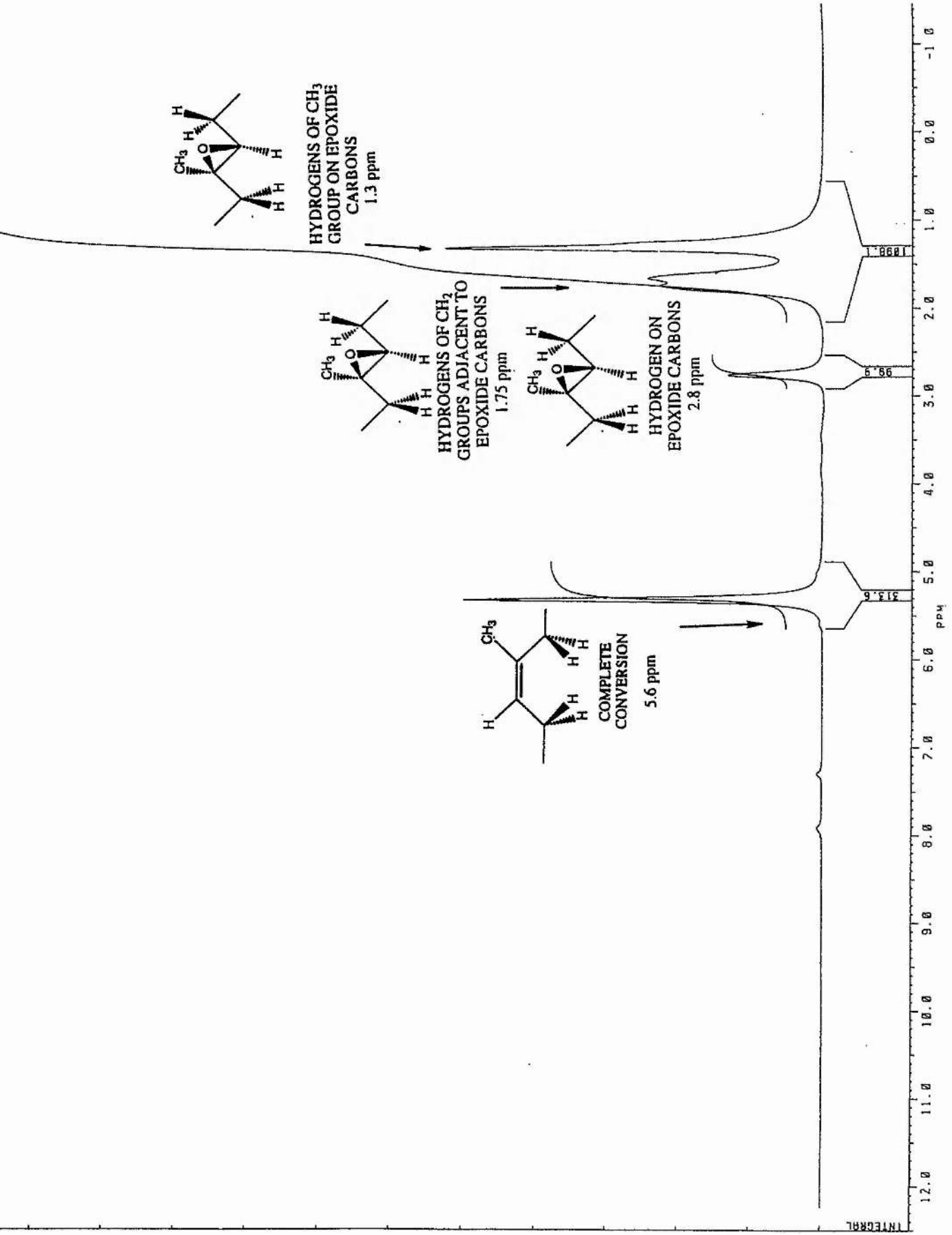
Spectrum 2.13

Purified Polyepoxide (LMWT-PBD) - ^{13}C NMR
with molecular sieves in CH_2Cl_2



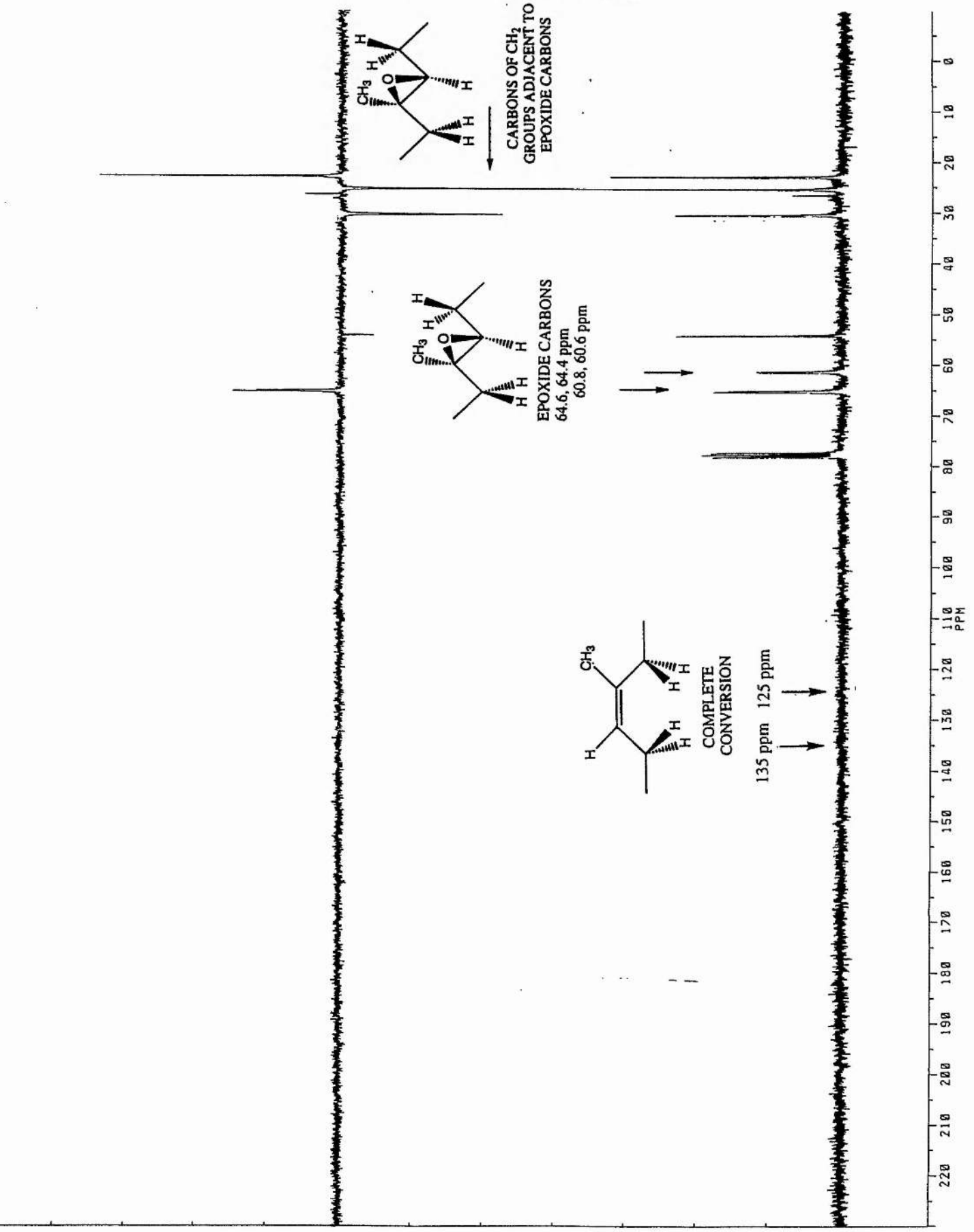
Spectrum 2.14

Purified Polyepoxide (LMWT-PISOP) - ^1H NMR
with molecular sieves in CH_2Cl_2



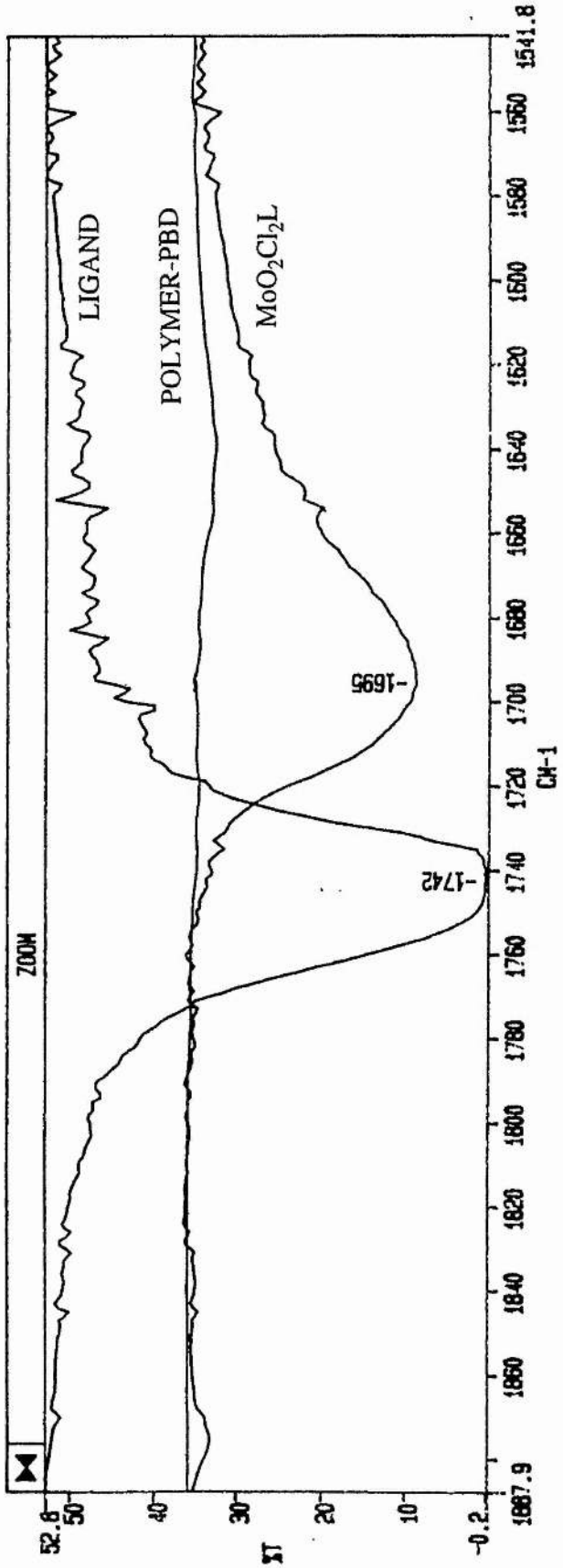
Spectrum 2.15

Purified Polyepoxide (LMWT-PISOP) - ^{13}C NMR
with molecular sieves in CH_2Cl_2



Spectrum 2.16

Polyepoxide (LMWT-PBD) - FTIR
with molecular sieves in CH_2Cl_2

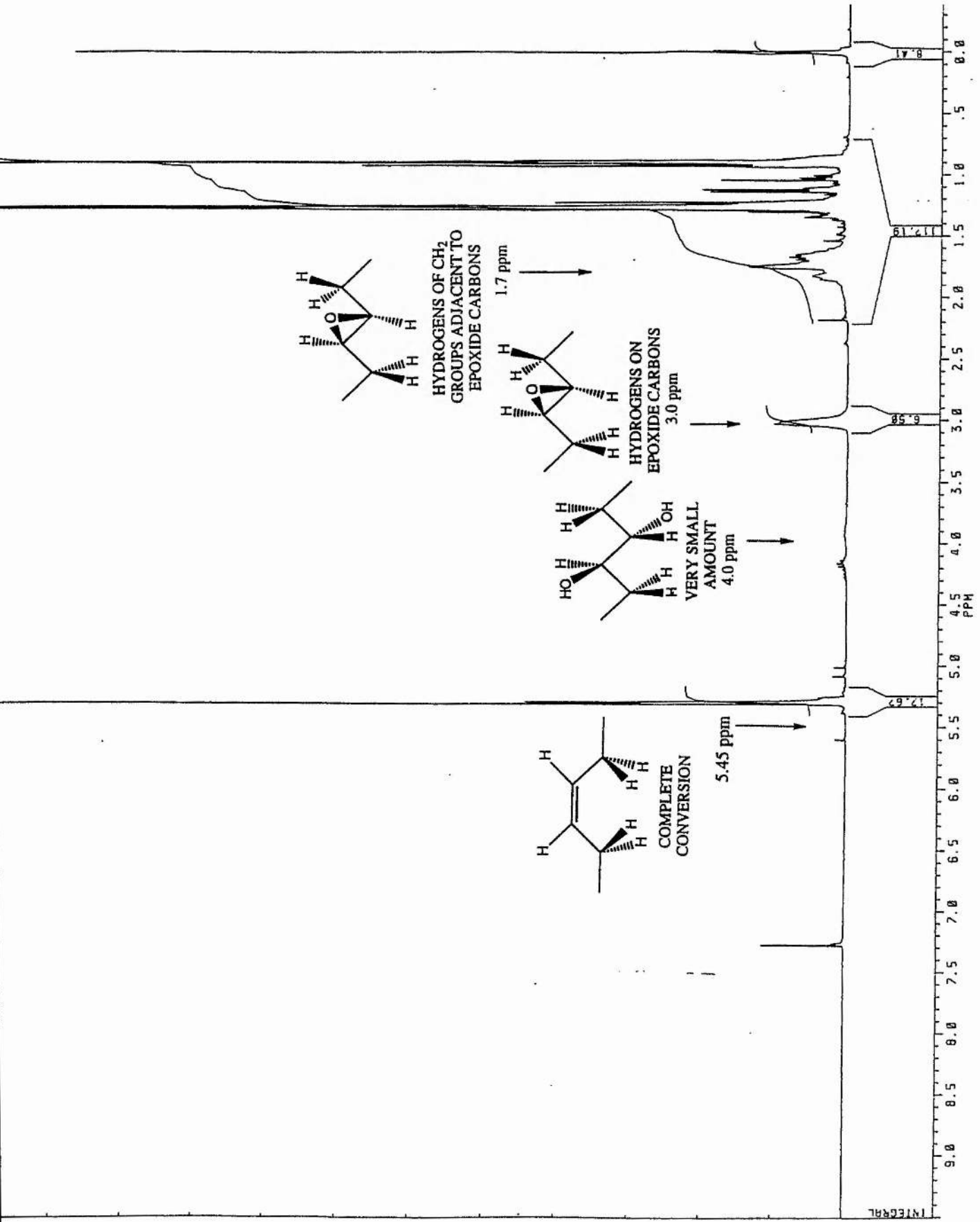


Spectrum 2.17

Polyepoxide (LMWT-PBD) - ^1H NMR

with molecular sieves in CH_2Cl_2.

Catalysed by Mo/Mol sieves catalyst

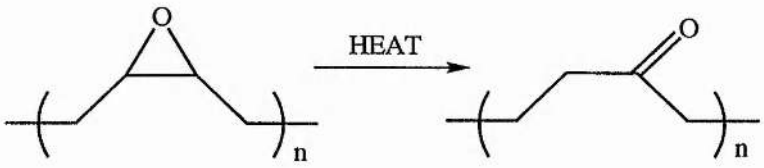


2.4.3 PHYSICAL AND THERMAL PROPERTIES OF POLYEPOXIDE

The purified polymers prepared with Mo-mol sieves catalyst have been studied by simultaneous thermal analysis (STA).

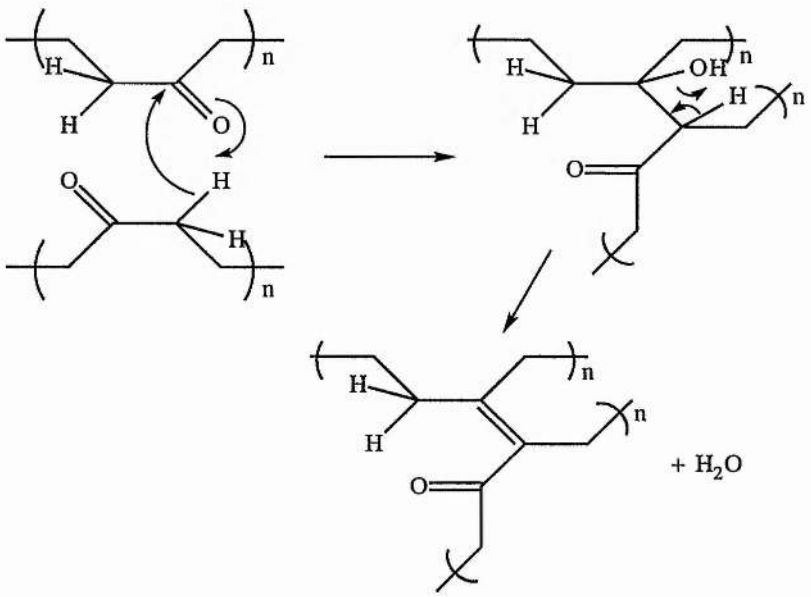
Purified polyepoxide of PISOP and PBD with Mo/Mol sieves catalyst in CH_2Cl_2.

Below 200°C the initially weight loss in the TGA of 10%, is exhibited by both polymers and can be assigned to the evaporation of solvent. Above 200°C, in both cases, an exotherm in the DTA (trace 2.1 and 2.2 on pages 86 and 87) is observed and has no accompanying weight loss, which is attributed to the isomerisation of the epoxide to the ketone, equation 2.4.



Equation 2.4: Isomerisation of the epoxide to a ketone with heat.

The ketonic groups then react with one another in an aldol condensation type reaction to form crosslinks between the polymer chains, this is support by a small exotherm in the DTA above 250°C accompanied by a 15% weight loss in the TGA. (Equation 2.5).



Equation 2.5: Crosslink of the polyketone via an aldol condensation reaction.

If all the epoxides in the polymer were to form ketones and they were all to crosslink, then for every crosslink there would be two epoxides units used and only one mole of water generated, therefore the percentage weight loss of the polymer would be 1mole of water/2 mole of epoxide x 100, supported by the following calculated and measured results which are similar.

For the polybutandiene (calculated): $\frac{18}{140}$ = 12.8%

From TGA curve(measured): 92-75 = 17%

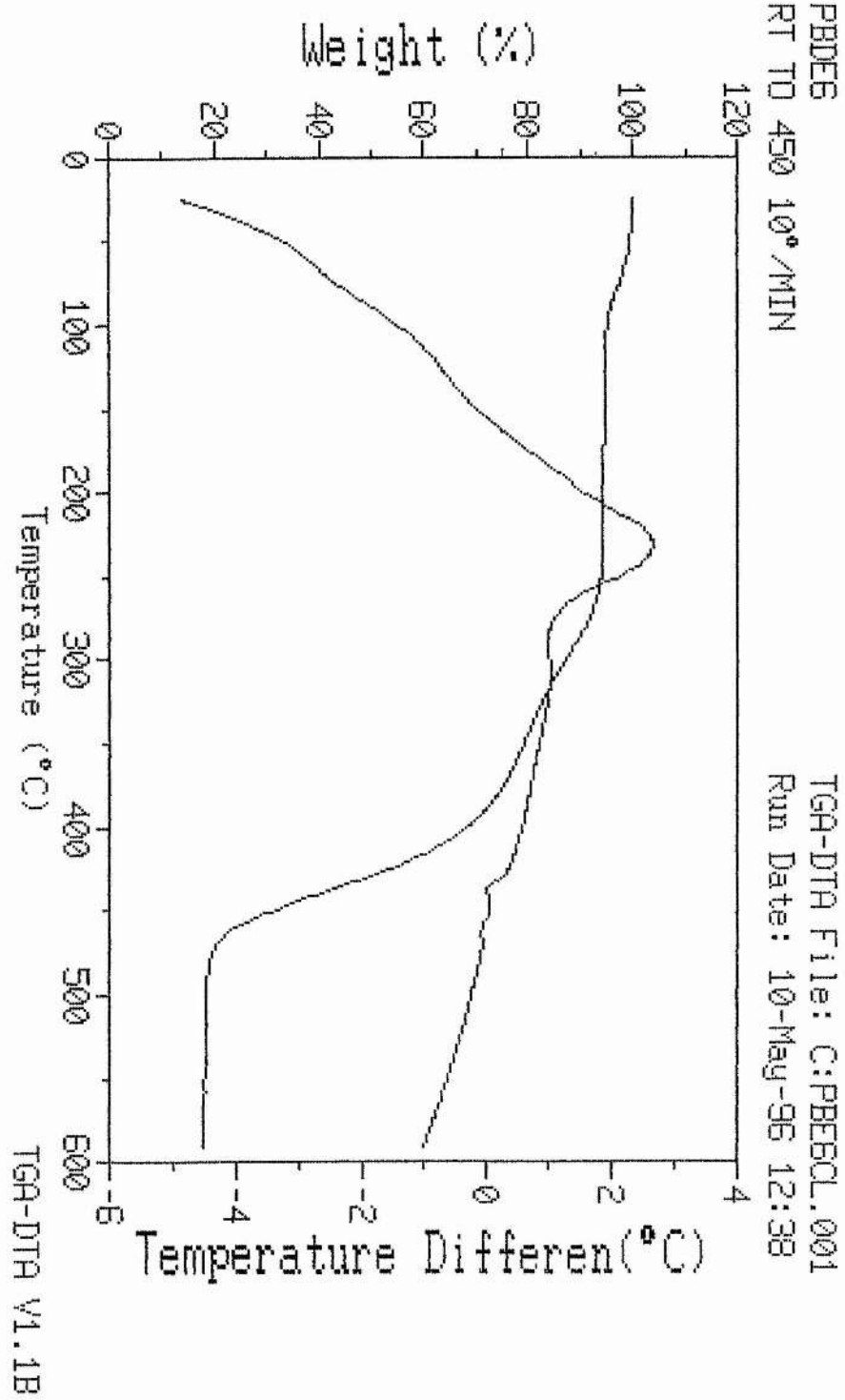
For the polybutandiene (calculated): $\frac{18}{168}$ = 10.7%

From TGA curve(measured): 91-78 = 13%

The finally weight loss in the TGA of both polymers and the accompanying ripple in the DTA is indicative of polymer decomposition.

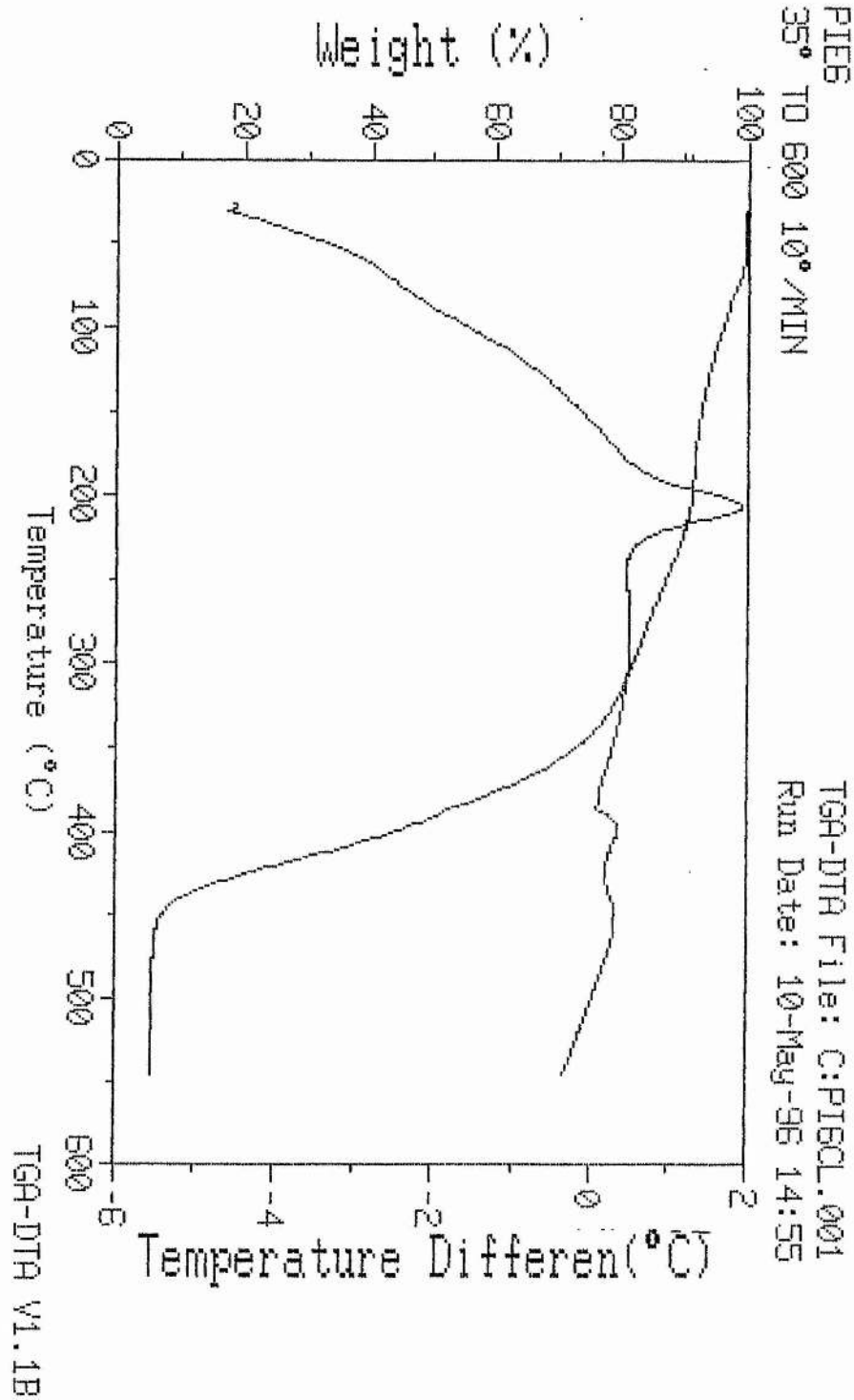
Trace 2.1

Polybutadiene epoxide - Mo/Mol sieve catalysed



Trace 2.2

Polyisoprene epoxide - Mo/Mol sieve catalysed



2.5. CATALYST STUDY

2.5.1 LOW TEMPERATURE NMR STUDIES OF THE [MoO_2Cl_2L]

The behaviour of the [MoO_2Cl_2L] catalyst[73] was investigated using low temperature NMR studies.[89] These studies provide information on the activities of this catalyst in the presence of the different reagents either singly or together. Most importantly these experiments were used to observe whether the diethoxyphosphoryl camphor ligand was removed by any of the reagents (other than molecular sieves) or if any other complexes were formed in the samples listed in the table below.

TABLE 2.7

LOW TEMPERATURE NMR ANALYSIS OF MOLYBDENUM CATALYST

SAMPLE	CONSTITUENTS	TEMPERATURE	FREE LIGAND[a] observed	CATALYST LIGAND[b] observed
CAT 1	MoO_2Cl_2L	-50°C	-	√
CAT 2	MoO_2Cl_2L	Room Temp	-	√
CAT 3	MoO_2Cl_2L + Bu^tOOH	-20°C	-	√
CAT 4	MoO_2Cl_2L + Bu^tOOH	-50°C	-	√
CAT 5	MoO_2Cl_2L + Bu^tOOH	Room Temp	-	√
CAT 6	MoO_2Cl_2L + CYCLOHEXENE	-50°C	-	√
CAT 7	MoO_2Cl_2L + CYCLOHEXENE	Room Temp	-	√
CAT 8	MoO_2Cl_2L + Bu^tOOH + CYCLOHEXENE	-50°C	-	√
CAT 9	MoO_2Cl_2L + Bu^tOOH + CYCLOHEXENE	-40°C	-	√
CAT 10	MoO_2Cl_2L + Bu^tOOH + CYCLOHEXENE	-30°C	-	√
CAT 11	MoO_2Cl_2L + Bu^tOOH + CYCLOHEXENE	-20°C	-	√
CAT 12	MoO_2Cl_2L + Bu^tOOH + CYCLOHEXENE	Room Temp	-	√

CAT - catalyst [MoO_2Cl_2L] study.

a - Resonance for the free ligand in the ^{31}P NMR at 23.1 ppm and in the ^1H NMR at 2.93 ppm.

b - Resonance for the cat. ligand in the ^{31}P NMR at 24.3 ppm and in the ^1H NMR at 3.71 ppm.

√ - ^1H and ^{31}P NMR indicated the presence of the catalyst ligand.

The results in the table above indicate that the organic ligand on the catalyst was not removed or displaced at any time in any of the above reactions, as the characteristic resonances for the free ligand [86] at 23.1 ppm in the ^{31}P NMR and 2.93 ppm in the ^{1}H NMR were not observed. The only characteristic resonances present for the ligand were those of the intact catalyst at 24.3 ppm in the ^{31}P NMR and 3.71 ppm in the ^{1}H NMR spectra, indicating that the molecular sieves were initially responsible for any free ligand observed in the epoxidation reactions. However after long reaction times (72 hrs), the catalyst in the presence of Bu^tOOH or Bu^tOOH and cyclohexene, showed evidence for the release of the free ligand.

Another resonance was observed in the ^{31}P NMR of $[MoO_2Cl_2L]$ + Bu^tOOH sample at -20°C and -50°C, which is believed to be a complex formed between the $[MoO_2Cl_2L]$ and the Bu^tOOH. A yellow precipitate was also observed, possibly a molybdenum complex but did not contain the camphor derived ligand when analysed by infrared.

2.5.2 CHLORIDE ANALYSIS ON $[MoO_2CL_2L]$ USING HPLC

It is known that molecular sieves bind to the molybdenum with the expulsion of the organic ligand and from the low temperature NMR studies it has been shown that the other reactants do not initially affect the catalyst, as no free ligand is observed. In order to have more information on the nature of the bound species, studies were carried out to discover whether Cl^- was released or remained bound to the molybdenum.

The reaction of the solution from the $[MoO_2Cl_2L]$ with molecular sieves was analysed by HPLC to observe if any chloride was lost during the reaction and if so, what reactants affected this. Therefore a set of reactions was carried out as shown in the table below:

TABLE 2.8

TABLE OF RESULTS FROM HPLC DETERMINATION OF CHLORIDE

REACTION	SOLVENT	MoO_2Cl_2L	MOLECULAR SIEVES	Bu^tOOH	AMOUNT OF CHLORIDE*
Cl 1	CH_2Cl_2	0.4g	-	-	NONE
Cl 2	CH_2Cl_2	0.4g	10 g	-	6.7 ppm
Cl 3	CH_2Cl_2	0.4g	10 g	8 cm^3	127.5 ppm

Cl - Determination of chloride released from catalyst.

* - Amount of chloride detected by HPLC, using a 100 ppm standard.

The reactions in the table above indicate that when molecular sieves are introduced, chloride is lost from the catalyst, supporting the evidence for the interaction with the metal centre. The presence of the oxidant Bu^tOOH increases the loss of chloride from the catalyst as can be seen from the chromatograms 2.1 and 2.2 (page 91) when compared with a 100 ppm

standard, chromatogram 2.3, on page 91. In general the chloride detection was quite low, 6.7 ppm for the reaction with molecular sieves and 127.5 ppm for the reaction with molecular sieves and Bu^tOOH, compared to the 1228 ppm chloride expected from the 0.4 g of the molybdenum catalyst.

Hence, it is possible to conclude from catalyst investigation that during epoxidation reactions with molecular sieves, the molecular sieves bind to the Mo metal centre with the expulsion of the organic ligand and free chloride. We can also be certain that the active molybdenum centres are bound on the surface rather than in the cavities of the molecular sieves since they are still active for epoxidation of polybutadiene with a molecular weight of 3×10^6, which is to large to enter the pores of the molecular sieves.

A plausible catalytic centre, which is consistent with all the data is shown below:

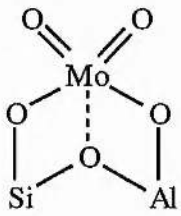


Figure 2.16: Possible catalytic centre for the epoxidation reactions of polybutadiene and polyisoprene.

Chromatogram 2.1
Detection of Chloride
Molecular Sieve and $[MoO_2Cl_2L]$

6.7 ppm

Chromatogram 2.2
Detection of Chloride
Molecular Sieves, $[MoO_2Cl_2L]$ and Bu^tOOH

127.5 ppm

Chromatogram 2.3
Detection of Chloride
100 ppm standard

2.6 CONCLUSIONS FROM EPOXIDATION OF THE POLYDIENES

Polybutadiene and polyisoprene can be easily converted to their respective polyepoxide. The backbone double bonds of the polydienes are converted with greater than 95% selectivity to the epoxide being achieved with no diol being formed. The conversion to the epoxide is directly affected by the presence of molecular sieves as it has been shown that the addition of molecular sieve improves the yield and the rate of the reaction. Conversion is much better in the presence of molecular sieves than without as they prevent the formation of a less active molybdenum catalyst possibly caused by the presence of adventitious water. It has been reported[84] that molecular sieves not only scavenge water but also bind the Mo catalyst and the Bu^tOOH and this has been supported by observations of the free ligand in reactions with molecular sieves and intact catalyst in those carried out in the absence of molecular sieves. It is proposed that the catalytic centre previously suggested is formed when the molecular sieves bind to the Mo metal centre with the expulsion of the organic ligand and free chloride. It is situated on the surface of the molecular sieves rather than in the cavities since it is still active for epoxidation of polybutadiene with a molecular weight of 3×10^6, indicating that it is too large to enter the pores of the molecular sieves.

The polyepoxides formed are easily purified after residual hydrochloric acid produced from the catalyst is removed using calcium carbonate. The polymer can be precipitated with petrol without fear of crosslinking, and will easily re-dissolve in CH_2Cl_2 or THF, although residual molybdenum metal remains in the polymer as indicated by atomic absorption. The amount of molybdenum is reduced in the alternative epoxidation method in which the molecular sieves and the molybdenum catalyst are stirred together in either THF or CH_2Cl_2. The solution containing free ligand and intact catalyst is then removed leaving only the molybdenum which is bound to the molecular sieves. This method is economically more viable as there are fewer impurities to remove after the reaction is completed and therefore less expensive.

CHAPTER THREE

ISOMERISATION

3.0 INTRODUCTION

3.1 ISOMERISATION OF POLYEPOXIDES TO POLYKETONES

The importance of polyketones as biodegradable polymers and structural materials led us to investigate the isomerisation of the polyepoxides by ring opening to form polyketones.

One of the most important polyketones, which has just been commercialised, is that derived from the alternating co-polymerisation of carbon monoxide and ethene.[25] This polymer has excellent properties in film forming, but the regularity of its structure means that it has crystalline domains which lead to a high melting point, which is close to its decomposition temperature. This, in turn, means that there are problems with processing the polymer. Generally, these are improved by adding propene to the feedstock so as to introduce some irregularity into the chain.

These polymers contain two carbon atoms between each carbonyl unit, and we reasoned that further advantages in terms of processing might be possible if this chain length were variable (2, 3 or 4 carbon atoms between each carbonyl group) or longer, increasing rotational degrees of freedom by having fewer sp^2 hybridised carbon atoms.

In principle, isomerisation of the polyepoxides in the epoxidised polybutadiene or polyisoprene should be able to provide polyketones of the type shown in figures 3.1 and 3.2.

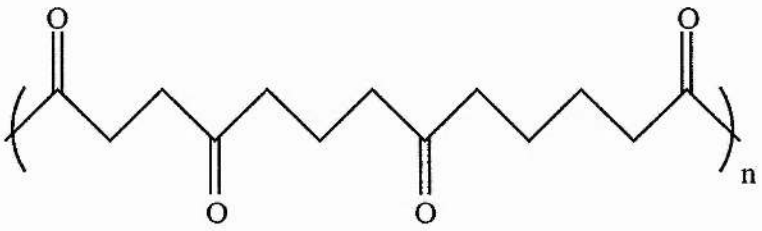


Figure 3.1: Possible polyketone structure obtained from *cis*-polybutadiene.

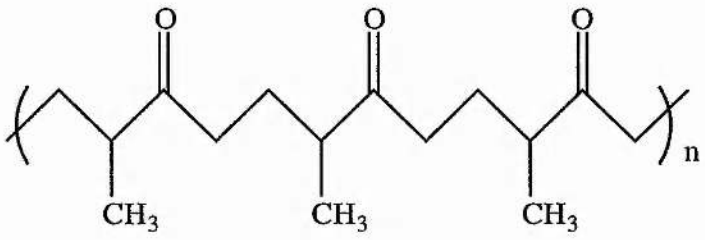


Figure 3.2: Possible polyketone structure obtained from polyisoprene epoxide.

In the case of the polybutadiene ketone (figure 3.1), the position of the carbonyl group will be irregular due to two sites being available at the double bond in the polybutadiene backbone (figure 3.3). Consequently the chain length between the carbonyl groups will vary

resulting in a polymer chain with carbonyl groups in 1,4, 1,5 and 1,6-positions producing an irregular polymer chain with additional degrees of freedom, which will disrupt the packing of the polymer chain and consequently the crystallinity giving rise to a more processable polymer.

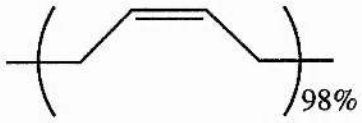


Figure 3.3: The structure for *cis*-1,4-polybutadiene.

Alternatively, the polyisoprene ketone (figure 3.2) will have a regular polymer chain due to the methyl group at the double bonds in the polyisoprene backbone as this leaves only one site available for the formation of a carbonyl group. The position of the ketone is fixed as methyl migration is unlikely. The branched methyl groups and the additional carbon atoms between the carbonyl groups may also disrupt the packing of the polymer chains reducing the crystallinity and melting point to give easier processability.

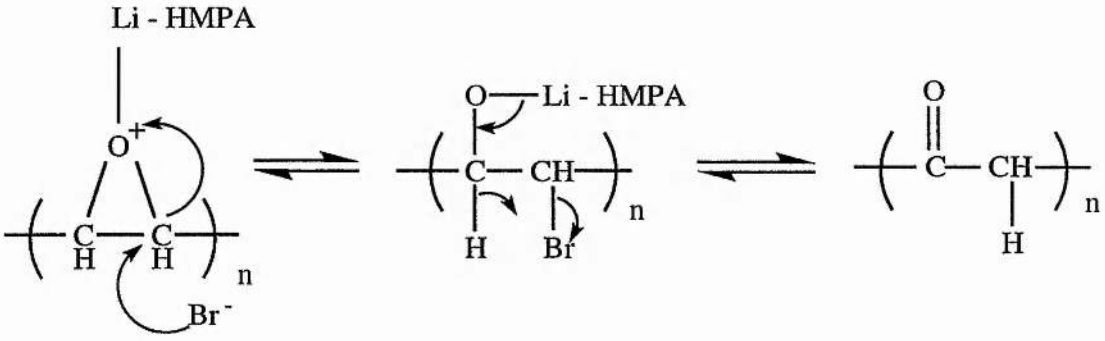
Related polymers have been synthesised before by direct oxidation of polybutadiene, but in all cases, the starting materials have contained pendant double bonds which oxidise preferentially to the backbone double bonds to give pendant methyl ketone units, although oxidation of the backbone double bonds is achieved after long reaction times.

Several catalysts are available for epoxide isomerisation, such as lithium cations, boron trifluoride etherate,[90] beryllium chloride in ether with silver tetrafluoroborate,[91] sodium iodide,[92] magnesium bromide,[93] $[RhCl(PPh_3)_3]$[94] and electrogenerated acid[95] but one of the most effective involves a 1:1 mixture of lithium bromide and hexamethylphosphoramide (HMPA) in benzene,[96] which we have studied for the isomerisation of the epoxidised polymers.

3.2 LITHIUM BROMIDE CATALYSED ISOMERISATION OF EPOXIDES

The lithium salt catalysed epoxide-carbonyl rearrangement has been studied by Rickborn and Gerkin.[96] They discussed the catalytic activity of LiBr with alkyl-substituted epoxides in benzene and the need for a solubiliser for lithium bromide, as this is insoluble in benzene. Rickborn and Gerkin found that the resultant complex was an efficient catalyst for the rearrangement of the epoxide to ketone. Product analyses presented for a number of simple cyclic and acyclic epoxides illustrate the scope for the reaction, which epoxides (e.g. 2,3-epoxypentane) with a structure similar to that of the polybutadiene epoxide are shown to be easily converted to the ketone.

The following reaction mechanism for solubilisers such as hexamethylphosphoramide (HMPA) and tri-n-butylphosphine oxide (n-Bu$_3$PO) was proposed.



Equation 3.1: Mechanism for lithium bromide isomerisation of an epoxide to a ketone.

In this mechanism the epoxide oxygen forms a complex with the Lewis acidic lithium cation. Bromide then attacks to give the lithium salt of the halohydrin.

A study of these reactions by Rickborn and Gerkin[96] involving the previously mentioned solubilising agents (in toluene or benzene) showed that the phosphine oxide exerts a marked solubilising influence on the salt, such that one mole of the salt was carried out into solution by one mole of the phosphine oxide (figure 3.4 on the next page) indicating that the phosphine oxide:LiBr ratio was important.

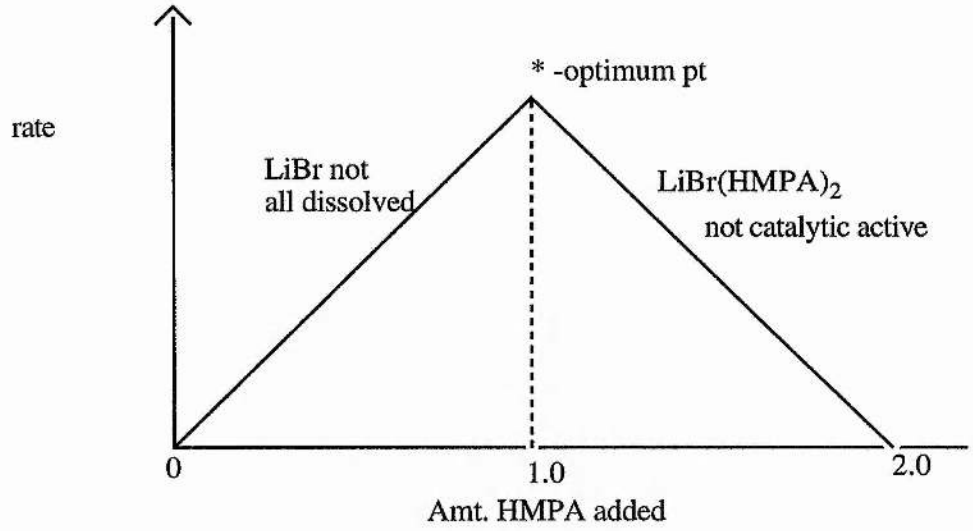


Figure 3.4: The effect of the ratio of HMPA:LiBr on the rate of ketone.

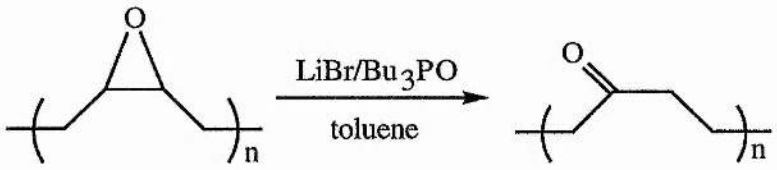
Optimum catalytic activity is achieved when the ratio of HMPA:LiBr is 1:1, where the lithium bromide is completely dissolved and no $(HMPA)_2Li$ (catalytically inactive) is produced.

The solubilising agent and lithium bromide can be easily removed by washing with water after the reaction is complete leaving a pure product.

We have applied this system to the isomerisation of epoxidised polybutadiene and polyisoprene polymers.

3.3 ISOMERISATION OF POLYBUTADIENE EPOXIDE

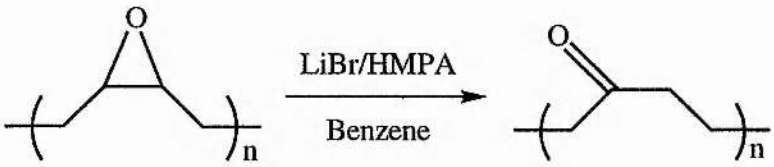
Initially, the unpurified polyepoxide (previously formed from *cis*-polybutadiene, M.W. = 2-3,000,000) was isomerised using tri-n-butyl phosphine oxide as the solubiliser and toluene as the solvent due to their availability, low toxicity and the fact that n-Bu_3PO complexes Li^+ in a similar manner to HMPA,[96] Equation 3.2.



Equation 3.2: Isomerisation of an epoxide to a ketone using lithium bromide/tri-n-butylphosphine oxide in toluene.

The isomerisation of the unpurified polyepoxide catalysed by lithium bromide in the presence of n-Bu_3PO and washed several times with water to remove any lithium bromide or n-Bu_3PO resulted in a soluble polymer. Since the desired polyketones are expected to be of low solubility either due to the highly crystalline nature of the polymer chains or possible crosslinking of the impure polyepoxide (containing acid units) via an aldol condensation type reaction, suggests that the reaction had not been successful. NMR and FTIR analysis of the isolated product suggested that some of the epoxide groups had reacted but that little or no carbonyl groups were formed.

As no carbonyl formation could be detected after several such reactions, n-Bu_3PO was replaced by hexamethylphosphoramide (HMPA) as the solubiliser. As HMPA is a highly carcinogenic compound it is necessary to implement the relevant safety procedures.



Equation 3.3: Isomerisation of an epoxide to a ketone
using lithium bromide/hexamethyl phosphoramide in toluene.

In this reaction type (Equation 3.3) two products were obtained, an insoluble polymer with a decomposition temperature in the range 146-148 ^oC; and a small residue obtained from the evaporated washings of the insoluble polymer.

3.3.1 SPECTROSCOPIC ANALYSIS OF INITIAL POLYKETONE PRODUCTS

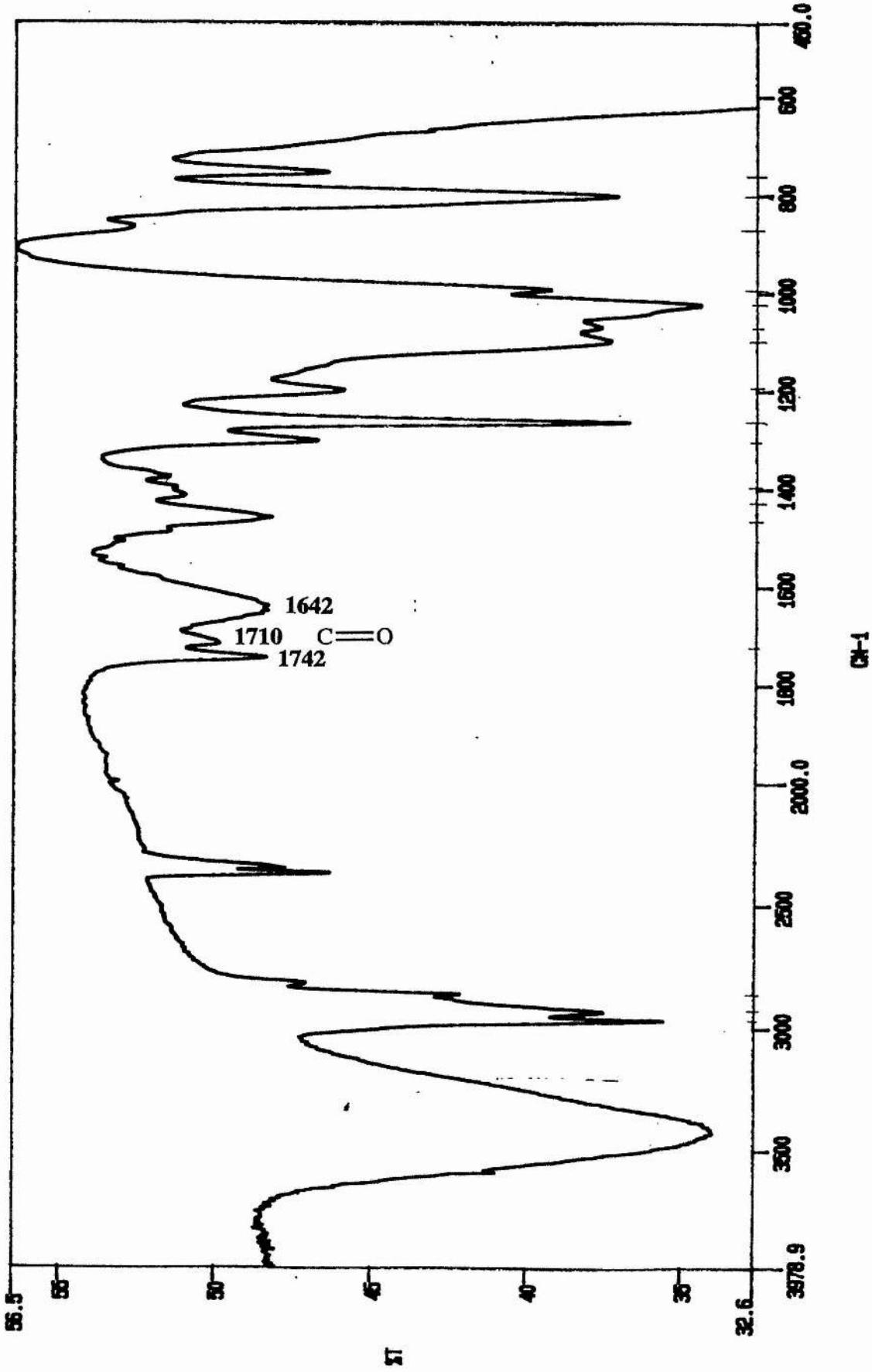
Infrared spectroscopy has given qualitative data for the introduction of a ketonic function into the polymer products obtained (spectrum 3.1 of the evaporated washings and spectrum 3.2 of the insoluble polymer on pages 99 and 100) from the isomerisation of the unpurified polybutadiene epoxide (PBD - M.W. 2-3,000,000) with HMPA / LiBr in benzene.

The characteristic carbonyl stretches for both polymer products are observed at about 1710 cm^{-1}, and the characteristic bands for the epoxide at 905 and 965 cm^{-1} are absent. The FTIR spectrum of the washings also shows bands at 1742 and 1250 cm^{-1} attributable to the camphor ligand used in the epoxidation. These are absent in the spectrum of the insoluble polymer indicating that the polymer is relatively uncontaminated with Mo complex and decomplexed ligand.

Spectrum 3.1

Polyketone (HMWT-PBD) - FTIR

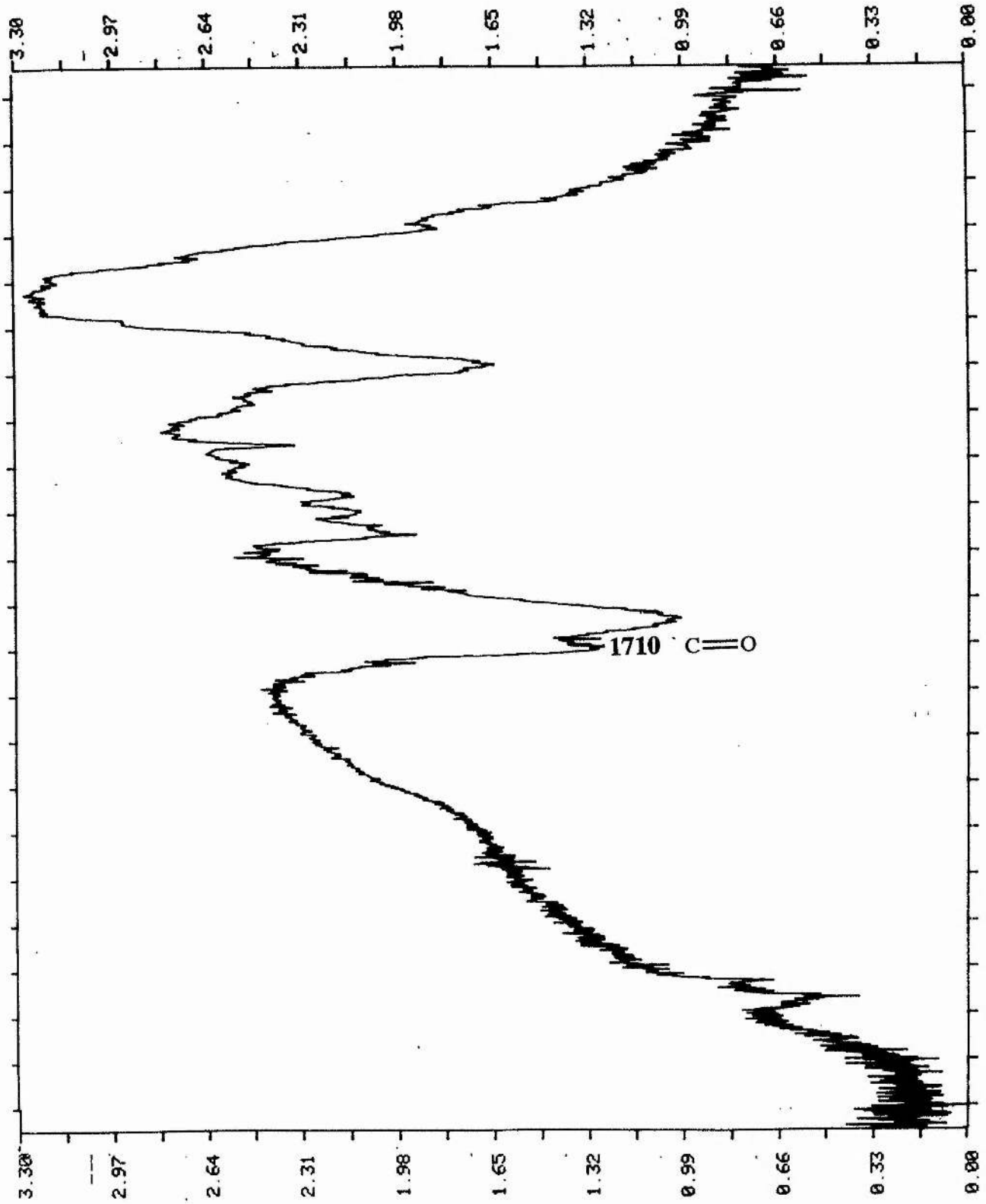
evaporated washings



Spectrum 3.2

Polyketone (HMWT-PBD) - FTIR

insoluble polymer

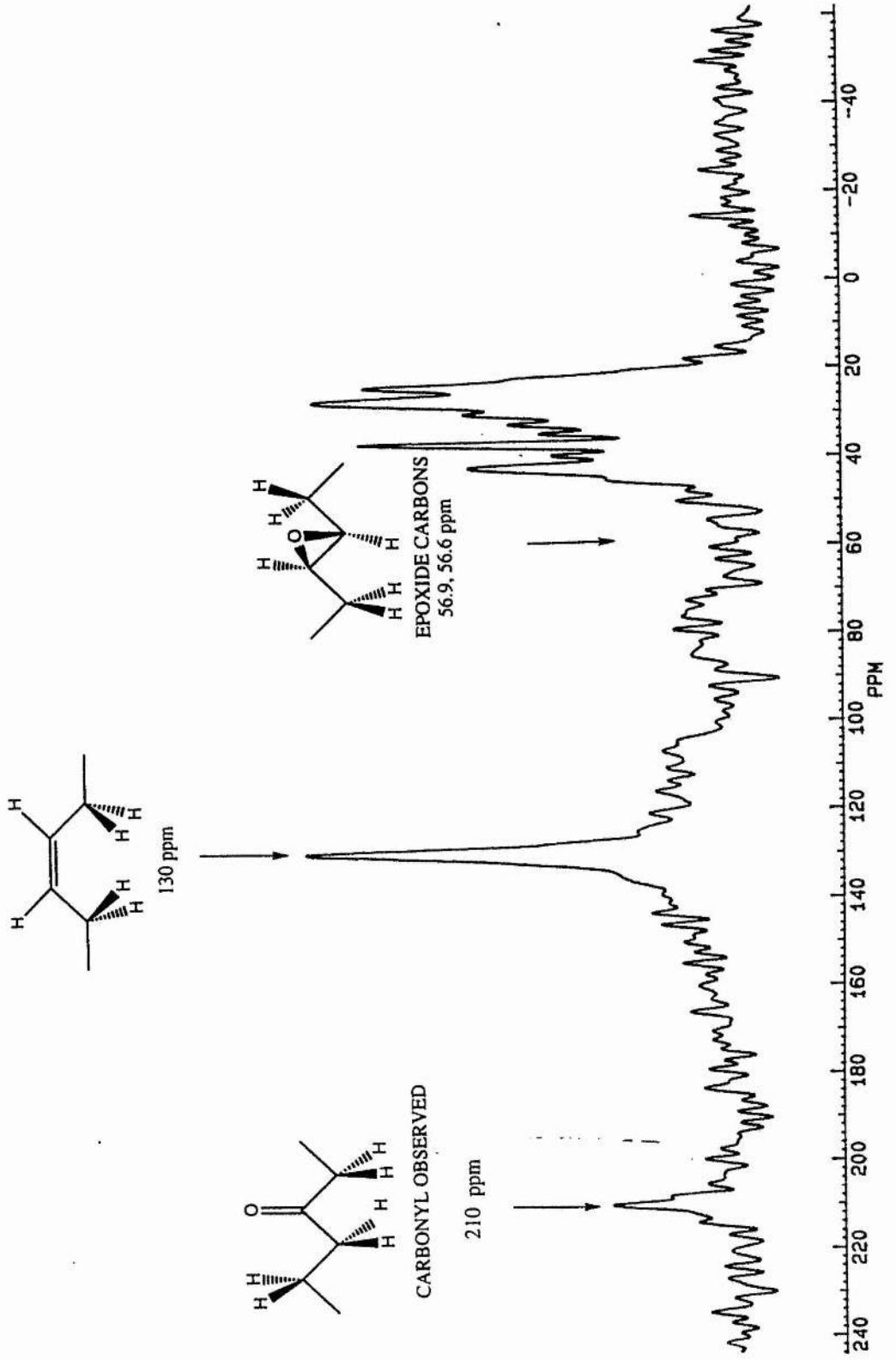


Further characterisation of the insoluble polymer using solid state NMR was attempted. Difficulties with packing the rotor caused problems with the spinning of the sample, but eventually a degree of rotation allowed the observation of a peak at 210 ppm, which is characteristic of a carbonyl group, supporting the previous observation made using infrared spectroscopy spectrum 3.3 page 102. There are no characteristic epoxide peaks at 56 ppm which suggests that all the epoxide groups in the polymer have been converted to ketonic groups. A peak at 130 ppm characteristic of double bonds is also observed, suggesting that there are double bonds in the final polymer product, which may have arisen from crosslinking via aldol condensation reactions. This, in addition to the high initial molecular weight of the polymer, may perhaps account for the low solubility of the product. It is also important to note that there is no evidence of hexamethylphosphoramide in this spectrum which would indicate that washing the polymer with water effectively removes the hexamethylphosphoramide and presumably the lithium bromide.

Spectrum 3.3

Polyketone (HMWT-PBD) - solid state ^{13}C NMR

solid polymer



3.3.2 CONCLUSIONS ON INITIAL ISOMERISATION REACTIONS OF POLYBUTADIENE EPOXIDE WITH LiBr/HMPA

Spectroscopic studies of these initial reactions have indicated that the lithium bromide catalysed epoxide-carbonyl isomerisation of polybutadiene epoxide has been successful in converting the epoxide groups in the epoxidised polybutadiene to ketone functionalities. Although the presence of double bonds in the final polymer product suggests crosslinking within the polymer matrix which would account for the insolubility of the polyketone formed, which will affect not only the purity of the polymer but also its characterisation via NMR and IR.

Reactions previously carried out with lithium bromide by Rickborn and Gerkin[96] indicated that the influence of the hexamethylphosphoramide was similar to that of the tri-n-butylphosphine oxide; however, in this particular case the hexamethylphosphoramide seems to be more effective.

3.3.3 SOLUBILITY OF THE POLYBUTADIENE KETONE

The solubility of the polybutadiene ketone has been investigated in many different ways starting from the most obvious, i.e. solvent systems which may dissolve the formed polyketone to changes in type and amount of substrate, solubilising agent and reaction solvent, utilising both model reactions and also those involving polymers, along with the derivatisation of the polyketone to polydioxolane,[97] which is known to be more soluble than the polyketone from which it originates.

3.3.3.1 SOLVENT INVESTIGATION FOR SOLUBILISING THE PREPARED POLYKETONE

The solubility of the solid polybutadiene ketone was investigated using a variety of solvents, table 3.1, all of which were unsuccessful in dissolving the polymer. However attempts to dissolve it in dimethyl sulphoxide and dimethyl formamide resulted in the polymer swelling which may indicate crosslinking of the polymer matrix during the isomerisation of the polyepoxide.

TABLE 3.1

SOLUBILITY OF POLYBUTADIENE KETONE IN VARIOUS SOLVENTS

	SOLVENTS	SUCCESS IN DISSOLVING POLYMER
1	Tetrahydrofuran	Polymer not soluble
2	Dimethyl formamide	Polymer swells
3	Dimethyl sulfoxide	Polymer swells
4	Toluene	Polymer not soluble
5	Methyl Ethyl Ketone	Polymer not soluble
6	Benzene	Polymer not soluble
7	α-butyrolactone	Polymer not soluble
8	Dichloromethane	Polymer not soluble
9	Chloroform	Polymer not soluble

Suitable solvents for a perfectly alternating polyketone (e.g. ethene-carbon monoxide copolymer) are m-cresol and hexafluoroisopropanol. m-Cresol initially looked promising as the polyketone seemed to partially dissolve. Therefore, a lithium salt catalysed isomerisation reaction was carried out using m-cresol as the solvent. Unfortunately, it was difficult to observe the carbonyl groups in the NMR spectrum possibly because the m-cresol signals are much stronger than those of the carbonyl groups, and if any signals were present they would have been masked by the m-cresol signals. Further attempts to re-dissolve the formed polybutadiene ketone proved unsuccessful as it was ascertained that the polybutadiene ketone was merely being smeared onto the surface of the glass reaction vessel.

Similarly, hexafluoroisopropanol had very little effect on dissolving the high molecular weight polybutadiene ketone. The inability of these solvents to dissolve the polyketone may be due to incompatibility of the solvent with the new polyketone or possibly crosslinking. A few crosslinks in a high molecular weight polymer (2-3,000,000) would greatly increase its molecular weight and render it insoluble, consequently the microstructure and molecular weight of the polybutadiene were investigated in an attempt to obtain a more tractable polymer. The starting molecular weight (2-3,000,000) is very high which may contribute to the problems.

3.3.3.2 REACTIONS OF POLYBUTADIENES WITH DIFFERENT MICRO STRUCTURES AND MOLECULAR WEIGHTS

The high molecular weight (2-3 x 10^6 amu) *cis*-1,4-polybutadiene (figure 3.5) used in the previous experiments causes problems with the solubility of the polybutadiene ketone formed and also the removal of the molecular sieves from the polybutadiene epoxide.

Figure 3.5: The microstructure for *cis*-1,4-polybutadiene.

In an attempt, therefore, to obtain a more soluble and tractable polyketone and facilitate easy removal of molecular sieves from the polyepoxide a series of epoxidation reactions was carried out with low molecular weight polybutadiene (LMWT-PBD) (Mn = 5,000) containing a *cis*/*trans*/vinyl (C/V/T) microstructure (figure 3.6) and also a lower molecular weight (2-300,000) *cis*-1,4-polybutadiene. Initially, the readily available C/V/T-polybutadiene was studied, however, the backbone double bonds in this polymer are preferentially epoxidised by the MoO_2Cl_2 (diethoxyphosphoryl camphor) catalyst leaving the pendant groups which can crosslink during isomerisation affecting the solubility of the polyketone. Later studies concentrated on LMWT-*cis*-polybutadiene as it has no pendant groups therefore crosslinking of this type is avoided.

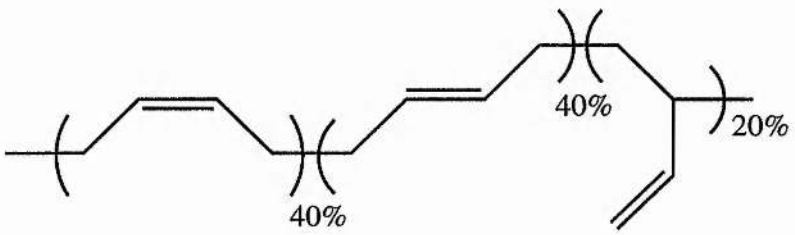


Figure 3.6: LMWT polybutadiene - *cis*/*trans*/vinyl microstructure

Reactions with the high molecular polybutadiene (HMWT-PBD) were used to obtain a comparison with the other lower molecular weight polymers (table 3.2).

TABLE 3.2

% CONVERSION TO EPOXIDE

	% CONVERSION IN EPOXID[n] RXNS			ISOMERISATION REACTIONS
REACTIONS with mol. sieves	EPOXIDE *cis/trans*	DIOL[e]	UNREACTED DOUBLE BONDS	EPOXIDE/ COMMENT
1a	90	10	NONE	epoxide reduced/ white solid noted
2a	**60**	40	NONE	epoxide reduced/ white solid noted
3b	60 / 60	40	NONE 100[d]	no polymer observed in NMR/ white solid noted
4b	66 / 63	47	NONE 100[d]	no polymer observed in NMR/ white solid noted
5b	**90 / 90**	14	TRACE 100[d]	no polymer observed / white solid noted
6c	**86**	14	NONE	epoxide reduced/ white solid noted
7c	**96**	4	NONE	white solid noted
8c	**>95**	-	NONE	white solid noted
9c	**>95**	-	NONE	white solid noted
10c	**91**	9	NONE	epoxide reduced white solid noted

a - HMWT *cis*-1,4-PBD (2-3 x 10^6 amu), 99% *cis* double bonds.

b - LMWT C/V/T-PBD (Mn = 5,000), 40% *cis*-1,4, 20% vinyl and 40% *trans*-1,4 double bonds.

c - LMWT *cis*-1,4-PBD (2-3 x 10^5 amu), 99% *cis* double bonds.

d - pendant double bonds in LMWT C/V/T-PBD.

e - High values of diol suggest the oxidant (Bu^tOOH) may be contaminated with water condensing from the atmosphere.

The polyepoxides from each polybutadiene were isomerised using LiBr/HMPA to give polyketones. Some of these isomerisation reactions were carried out in dichloromethane (solvent from epoxidation reaction) (highlighted in the table 3.2 in bold) as problems were encountered with redissolving the polyepoxide in benzene.

The low molecular weight polybutadiene polymers enabled easy removal of the polyepoxide solutions from the molecular sieves; however, solid polyketones were observed in

reactions involving both high and low molecular weight polybutadienes, all of which were analysed by FTIR and discussed below.

3.3.3.3 SPECTROSCOPIC ANALYSIS OF THE POLYBUTADIENE KETONES

The crude epoxide obtained for the epoxidised polybutadienes indicated that the LMWT *cis*-1,4-polybutadiene was more successful than the other polybutadienes (all carried out in the presence of sieves) in obtaining repeatedly high percentage conversions (>95%, table 3.2) to the epoxide with only a low percentage of diol being formed.

Subsequent isomerisation of the epoxidised polymers produced an insoluble solid polyketone in every case, and when analysed by infra-red spectroscopy each polymer showed the formation of characteristic carbonyl groups at 1710 cm^{-1} (spectrum 3.4 of LMWT-*cis*-PBD on page 108).

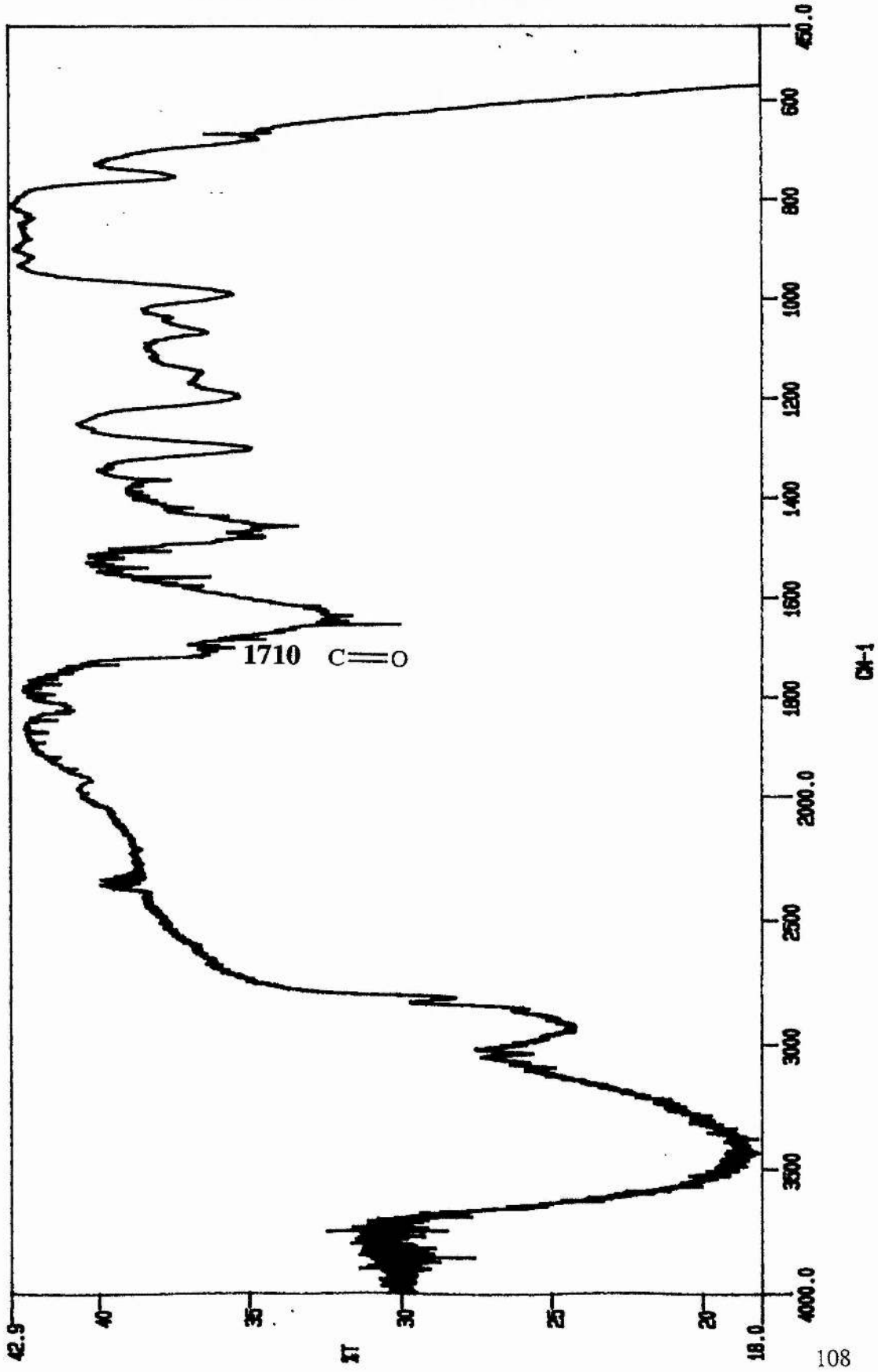
The ^{1}H and ^{13}C nmr spectra of the solutions obtained from an isomerisation reaction of LMWT-*cis*-polybutadiene epoxide, after removal of the insoluble material by filtration are shown in Spectra 3.7 and 3.8. They are compared with those of the starting polyepoxide (spectra 3.5 and 3.6). The spectra of the polyepoxide shows no unreacted double bonds and very little diol, with a peak area less than 10% of the epoxide. The product solution contain fewer epoxide units relative to the diol present (ratio approximately 1:1) suggesting that some of the epoxide units have been isomerised. Characteristic carbonyl resonances are not, however, observed near 200 ppm. In most cases no diol is present in the epoxide so it is impossible to tell from the solution NMR spectra whether or not isomerisation of this epoxide has occurred.

The isomerisation reaction was further investigated using polybutadiene with the LMWT *cis*-1,4-microstructure as this allows easy removal of molecular sieves and avoids the possible crosslinking via pendant group.

Spectrum 3.4

Polyketone (LMWT-*cis*-PBD) - FTIR

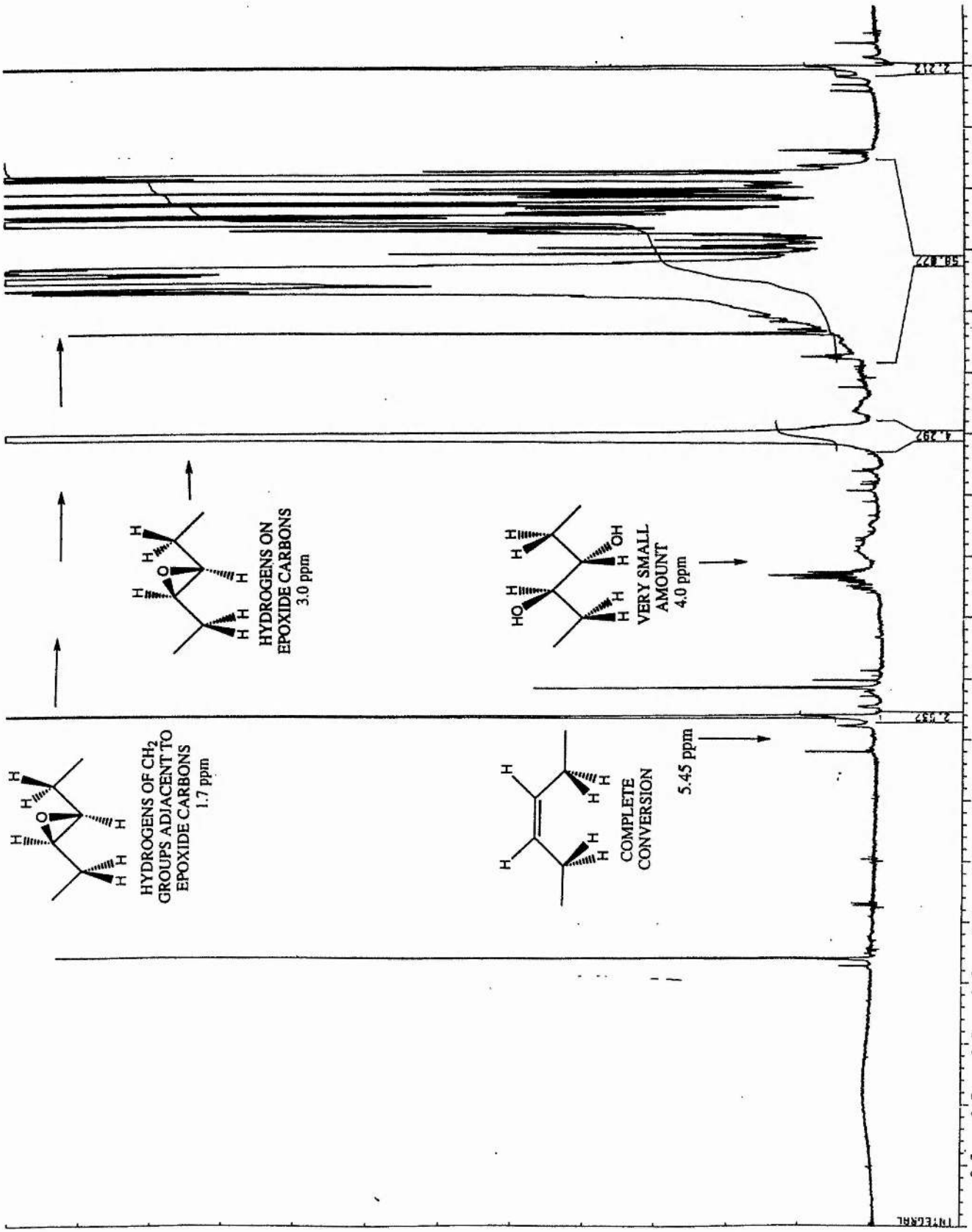
with molecular sieves - solid polymer



Spectrum 3.5

Polyepoxide (LMWT-*cis*-PBD) - Sample 8c - ^{1}H NMR

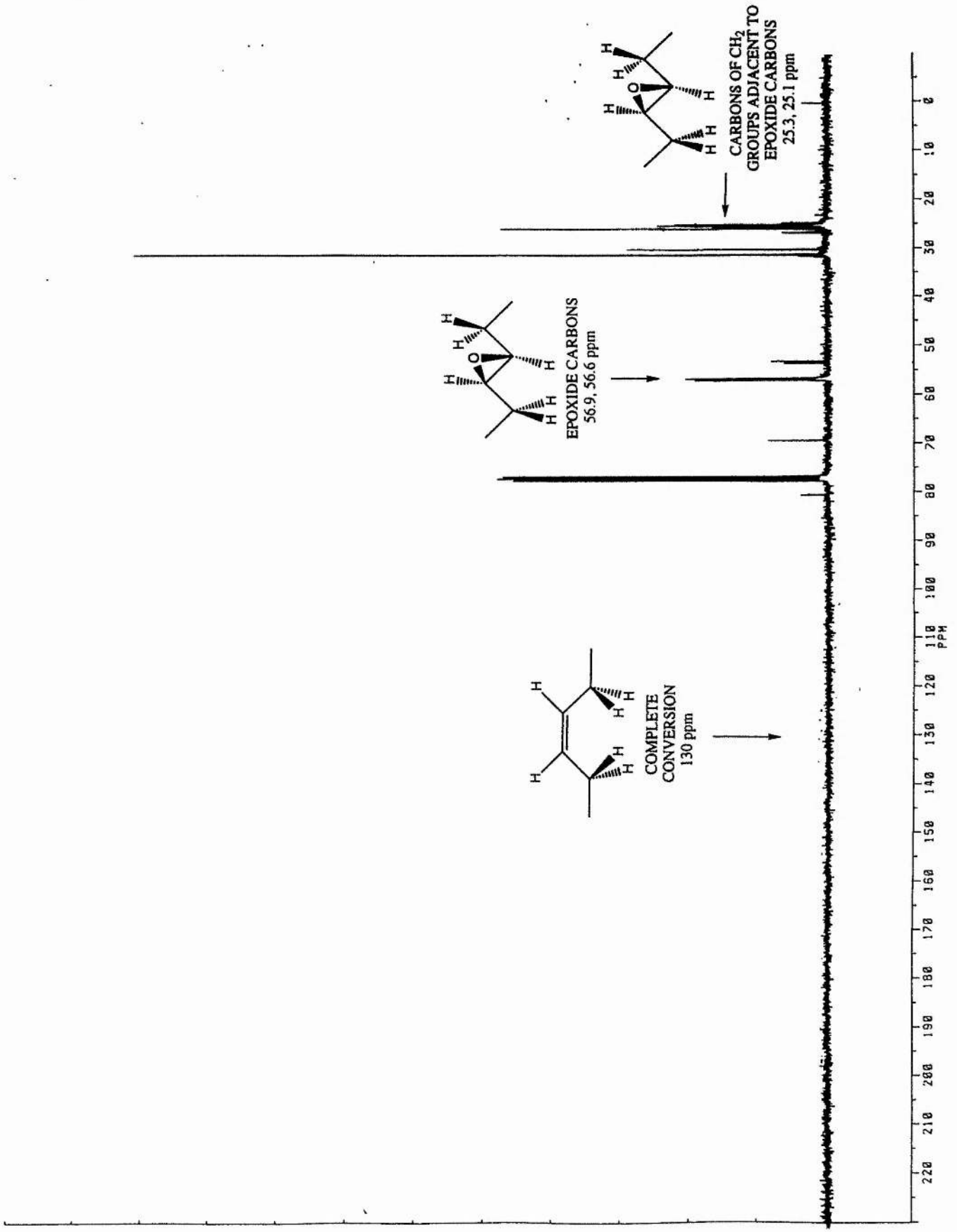
Epoxidation in the presence of molecular sieves resulting >95% conversion to the epoxide.



Spectrum 3.6

Polyepoxide (LMWT-*cis*-PBD) - Sample 8c - ^{13}C NMR

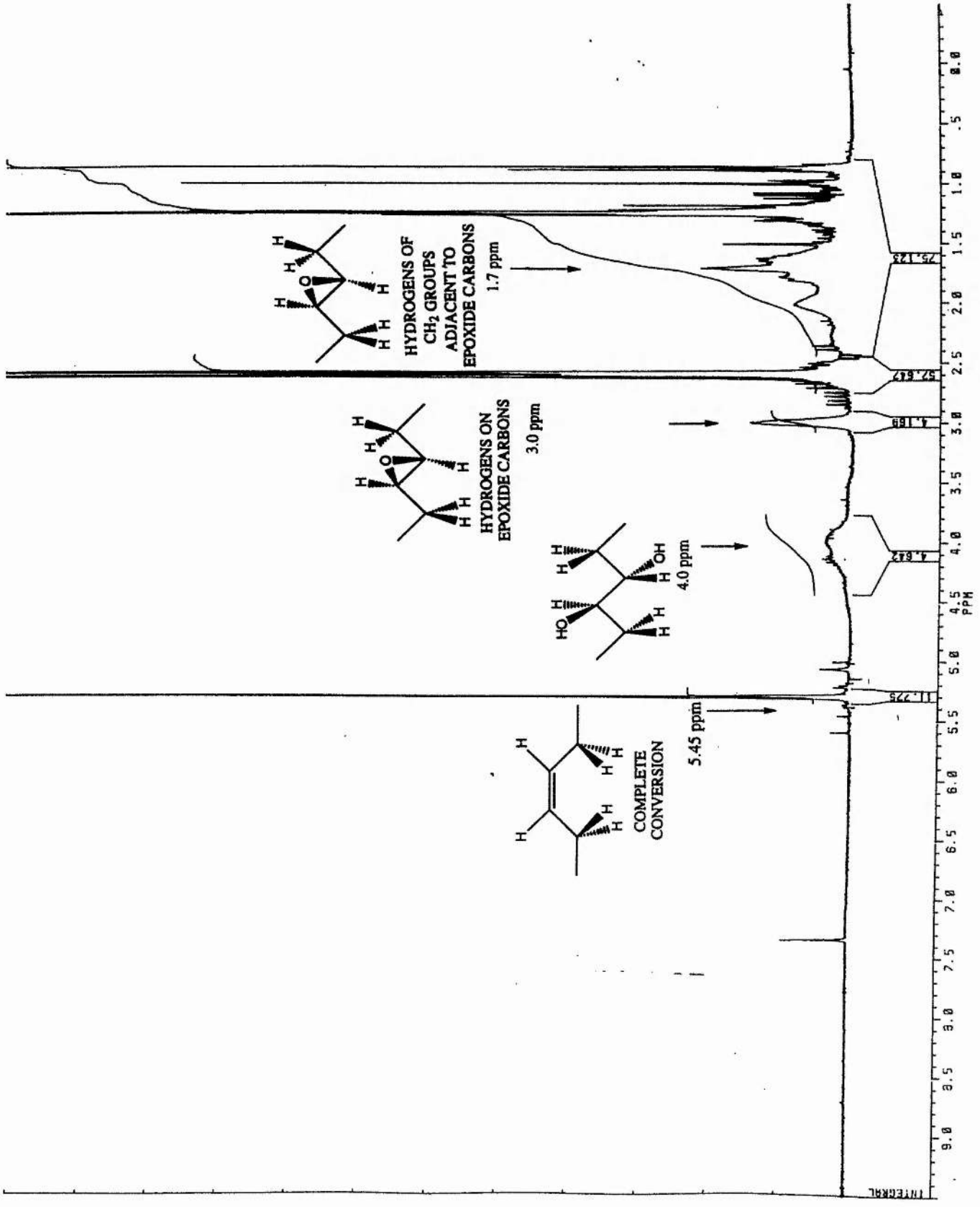
Epoxidation in the presence of molecular sieves resulting in >95% conversion to the epoxide.



Spectrum 3.7

Polyketone (LMWT-*cis*-PBD) - Sample 8c - ^{1}H NMR

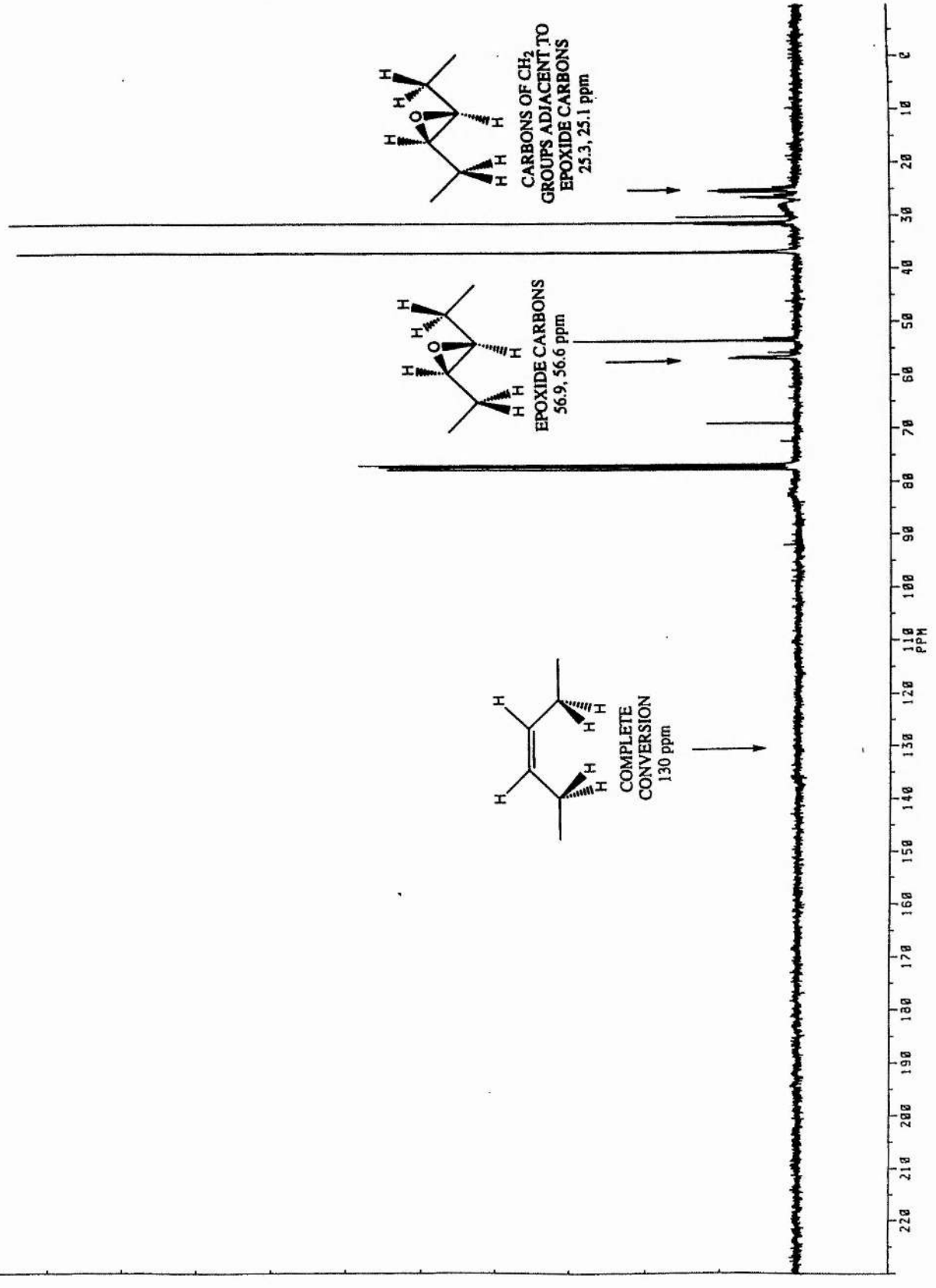
Isomerisation of polyepoxide (95%) with lithium bromide and HMPA.



Spectrum 3.8

Polyketone (LMWT-*cis*-PBD) - Sample 8c - ^{13}C NMR

Isomerisation of polyepoxide (95%) with lithium bromide and HMPA.



3.3.3.4 EFFECT OF LiBr POLYEPOXIDE RATIO ON SOLUBILITY

Polyepoxides of LMWT-*cis*-PBD with high percentages of epoxide groups and no double bonds were isomerised with various amounts of lithium bromide in the presence of HMPA (LiBr:HMPA = 1:1) table 3.3.

TABLE 3.3

% CONVERSION TO EPOXIDE AND KETONE FORMATION

(varying the lithium bromide : polymer ratio)

		%CONVERSION FOR EPOXID^n RXNS				
EPOXID^n RXN^a	MOLECULAR SIEVES	EPOXIDE *cis*	DIOL	UNREACTED DOUBLE BONDS	ISOMER^n RXN	RATIO OF LiBr:PE
1^b	√	79	21	NONE	1A	5:1
					1B	3:1
2	√	91	8	NONE	2	1:1
3^b	√	74	26	NONE	3A	1:2.5
					3B	1:5

a - Starting material was polybutadiene with 99% *cis double* bonds (M.W. = 2-300,000)

b - Polyepoxide was split into two samples A and B for the isomerisation reaction.

Note: Lithium bromide : HMPA -> 1:1

Solid products obtained from the isomerisation of the epoxide from polybutadiene show the presence of ketone groups at 1710 cm^{-1} in their infrared spectra, suggesting that the resultant insoluble products are polyketones.

Although the NMR analysis of these reactions did not show direct evidence of carbonyl formation (no ^{13}C NMR resonance near 200 ppm) they indicated significant differences in the amount of epoxide converted by comparing the diol/epoxide integrations for the polyepoxide with those of the polyketone as discussed earlier, see page 107.

In general it was observed that reactions with less than stoichiometric amounts of lithium bromide showed incomplete conversion of the epoxide groups, and the higher the level of lithium bromide the greater the conversion of epoxides, until a stoichiometric amount was used which gave complete conversion, consequently additional lithium bromide had no effect.

3.3.3.5 ISOMERISATION REACTION WITH ONLY LITHIUM BROMIDE

Literature concerning lithium salt catalysed isomerisation of monoepoxides[96,98] indicated the need for a solubilising agent such as HMPA. However, earlier experiments indicated that the lithium bromide partially dissolved (before the addition of the HMPA) in the polymer solution. A white polymer solid obtained from an isomerisation reaction with only LiBr, showed characteristic carbonyl resonances in the infra-red, see spectrum 3.9 on page 116, indicating that the isomerisation reaction had occurred without the HMPA solubiliser.

Subsequently, polyepoxides with a high percentage of epoxide groups, little or no diol and no double bonds were isomerised in the absence of HMPA, table 3.4.

TABLE 3.4

% CONVERSION TO EPOXIDE AND KETONE FORMATION

(with only lithium bromide)

		% CONVERSION IN EPOXID[n] RXNS			COMMENT ON
REACTION	MOLECULAR SIEVES	EPOXIDE *cis*	DIOL	UNREACTED DOUBLE BONDS	ISOMER[n] RXN
1a	√	>95	NONE	NONE	C=O[b], white.solid
2a	√	>95	NONE	NONE	C=O[b], white.solid
3a	√	>95	NONE	NONE	C=O[b], white.solid
4a	√	>95	NONE	NONE	C=O[b], white.solid
5a	√	82	18	NONE	C=O[b], white.solid

a - Starting material was polybutadiene with 99% *cis* double bonds
(M.W. = 2-300,000)
b - The carbonyl was observed in the infrared spectra at 1710 cm^{-1}.

In each reaction the lithium bromide was partially dissolved in the polymer solution, however after a few minutes a solid was formed. Characterisation by infrared spectroscopy indicated a carbonyl band at 1710 cm^{-1} for the solid products confirming the presence of ketonic functions within the polymer (see spectrum 3.9 on page 116). Further analysis of these products by solid state NMR was not possible as the sticky rubber consistency of the polymer would not allow it to be packed into the rotor.

Partial solubility of the lithium bromide in the polymer solution and observation of ketonic bands in the infrared may be a result of the polymer chelating to the lithium, Figure 3.7, with the lithium ions binding to the epoxide or ketonic oxygen atoms. Binding of this kind has been observed directly in solution of lithium salts in polyethyleneglycols. In these systems the lithium ions bind to the either oxygen atom and migration along the chain allows them to be excellent polymer electrolytes.

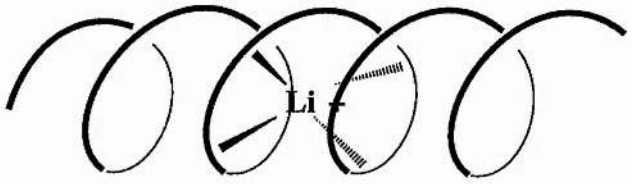


Figure 3.7: The polymer chelating to the lithium cation.

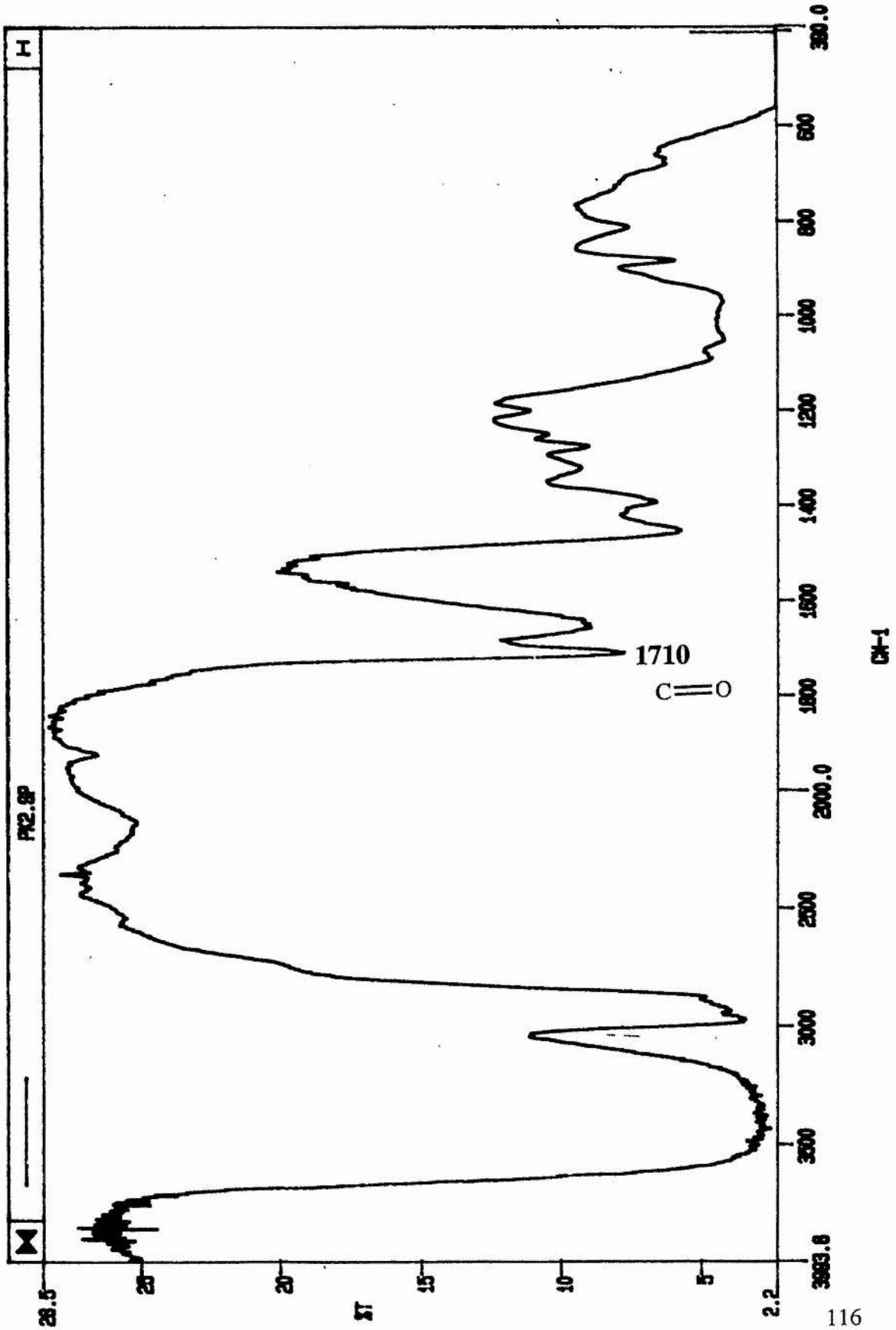
This interaction between LiBr and the polyketone was investigated using a model compound (2,5-hexanedione) refluxing it for 3 hours with lithium bromide in dichloromethane, in which the lithium bromide partial dissolved. A shift in the carbonyl resonance from 207.5ppm to 208 ppm for 2,5-hexandione confirmed the interaction between the lithium and the polymer.

The polymer, in dissolving the lithium bromide, renders the solubilising agent HMPA redundant. However, in reactions carried out in the absence of HMPA the removal of the lithium bound within the polymer was difficult. Attempts to remove the lithium from within the polymer after isomerisation using solubilising agents such as dimethylpropene urea (DMPU), dimethylimidazolidinone (DMI) and hexamethylphosphoramide (HMPA.) were not successful. Due to solubility problems of the polyketone the isomerisation of the polyepoxides were investigated via reactions of model compounds, discussed later. see page 122.

Spectrum 3.9

Polyketone (LMWT-PBD) - FTIR

solid polymer



3.3.3.6 ISOMERISATION OF POLYBUTADIENE EPOXIDE WITH DIFFERENT SOLUBILISING AGENTS AND SOLVENTS

Model reactions (discussed later) involved the study of 2,3-epoxybutane with DMI and HMPA as solubilising agents. These reactions indicated that both DMI and HMPA were effective in dissolving the lithium bromide. As a consequence the isomerisation reactions involving polybutadiene epoxide were carried out using DMI and HMPA as solubilising agent in reaction solvents benzene and dichloromethane. In addition, reactions with THF alone were carried out as this dissolves lithium bromide without the need for a solublising agent, table 3.5.

TABLE 3.5

TABLE OF COMPONENTS USED IN EACH ISOMERISATION REACTION AND THE RESULTS

RXN NUMBER	SOL AGENT	SOLVENT	% CONVERSION FOR EPOXID^{n} RXN		ISOMER^{n} RXN
			EPOXIDE	DIOL	COMMENT
1[a]	HMPA	Benzene	>95	-	white solid C=O at 1710 FTIR
2[a]	DMI	Benzene	>95	-	white solid C=O at 1710 FTIR
3[a]	HMPA	CH_2Cl_2	>95	-	white solid C=O at 1710 FTIR
4[a]	DMI	CH_2Cl_2	77	23	white solid C=O at 1710 FTIR
5[a]	NONE	THF	obs in ^{13}C	not obs due to THF	white solid C=O at 1710 FTIR
6[a]	NONE	THF	obs in ^{13}C	not obs due to THF	SOLUBLE POLYKETONE + white solid C=O at 1710 FTIR
7[b]	HMPA	CH_2Cl_2	35	65	white solid C=O at 1710 FTIR
8[b]	DMI	CH_2Cl_2	60	40	white solid C=O at 1710 FTIR

a - polybutadiene epoxide prepared with molecular sieves.
b - polybutadiene epoxide prepared without molecular sieves.

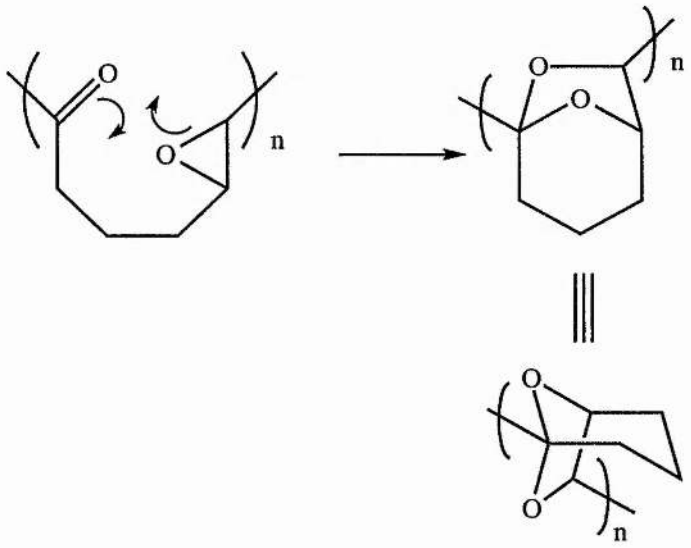
The polyepoxides prepared with molecular sieves give a good conversion to the epoxide of up to 95%, little or no diol formation and complete conversion of the backbone double bonds. However, those carried out without molecular sieves showed percentage conversion to the epoxide of 35% and 60%, and a high percentage of diol, 7b and 8b.

Unfortunately, the effect of the solubilising agents used to dissolve the lithium bromide in the polymer solution could not be compared directly as the reaction solutions showed no

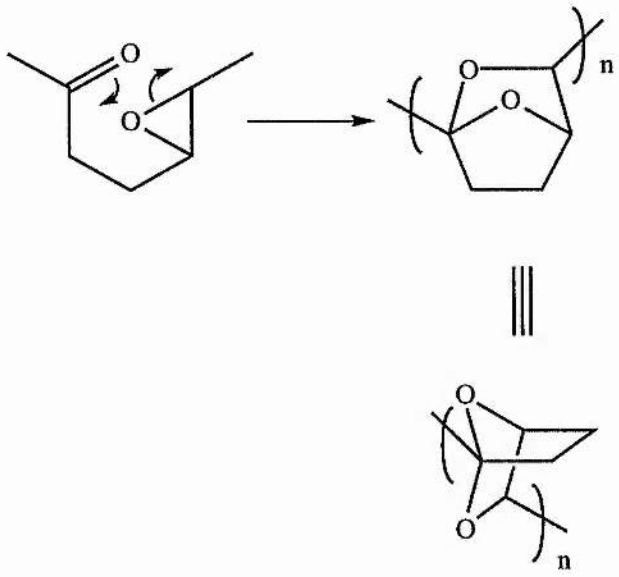
characteristic carbonyl formation in the NMR spectra of samples with or without molecular sieves. However, qualitative confirmation was obtained from infrared spectra of the solid polymers, which were washed with water to remove any solubilising agent or lithium bromide, these showed characteristic carbonyl bands at 1710 cm^{-1}, spectrum 3.10 on page 120.

Reaction products obtained are similar for all the reactions with lithium bromide using either DMI or HMPA in either benzene or CH_2Cl_2. The role of the HMPA or DMI is to solubilise the lithium bromide, but since lithium bromide dissolves in THF without a solubilising agent, reactions with THF alone were carried out. One of these reactions gave a soluble product which indicated the formation of characteristic carbonyl resonance at 203 ppm indicating the formation of ketone functionalities in the polymer chain, spectrum 3.11 on page 121.

In addition, there are six resonances near 100 ppm, in the region in which acetal or ketal carbon atoms resonate. There are two possible explanations for these resonances, firstly, they may be due to a soluble impurity which appears to be more concentrated in the polyketone than in the polyepoxide solution (see spectrum 2.8, page 67) because some of the polymer has precipitated out. Alternatively, some of these resonances may be associated with products obtained from ring opening or oxidation of THF (e.g. ɣ-butyrolactone is a product, see page 128) and others associated with the polymer. The NMR resonances associated with the polymer are those which occur between 100 and 105 ppm, similar to those of brevicomin type moieties.[99] Brevicomin type units may be generated within the polymer chain via a reaction between ketone and neighbouring epoxide units in the polymer.(Equation 3.4 and 3.5).[100]



Equation 3.4: The formation of brevicomin type, 6-8-dioxobicyclo [3.2.1] octane system.



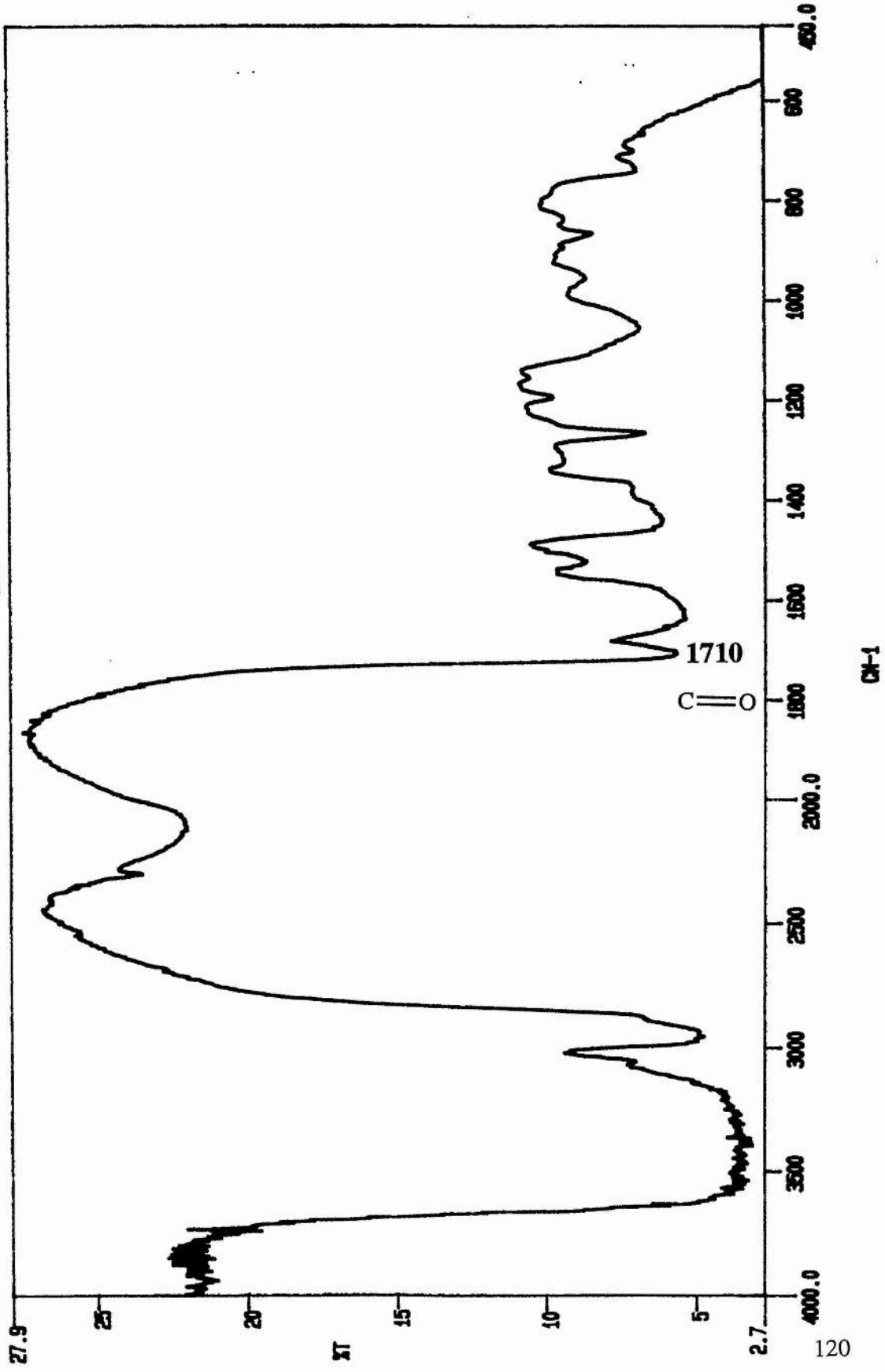
Equation 3.5: The formation of brevicomin type ring system
5-7-dioxobicyclo [2.2.1] heptane system

The opening of the epoxides presumably occurs in a random fashion along the polymer chain and the brevicomin type units can only occur when a ketone, or the alkoxide intermediate, is formed on the unit next to an intact epoxide. In the early stages of the reaction, this will normally be the case, but later on, the random nature of the reaction means that some epoxide units will become isolated between brevicomin type units. These will either oxidise to isolated ketone units, which will remain as ketones or may be too sterically hindered to be attacked. More than one resonance is observed for each type of unit (ketone, brevicomin and epoxide), suggesting a complex microstructure for the polymer.

Spectrum 3.10

FTIR

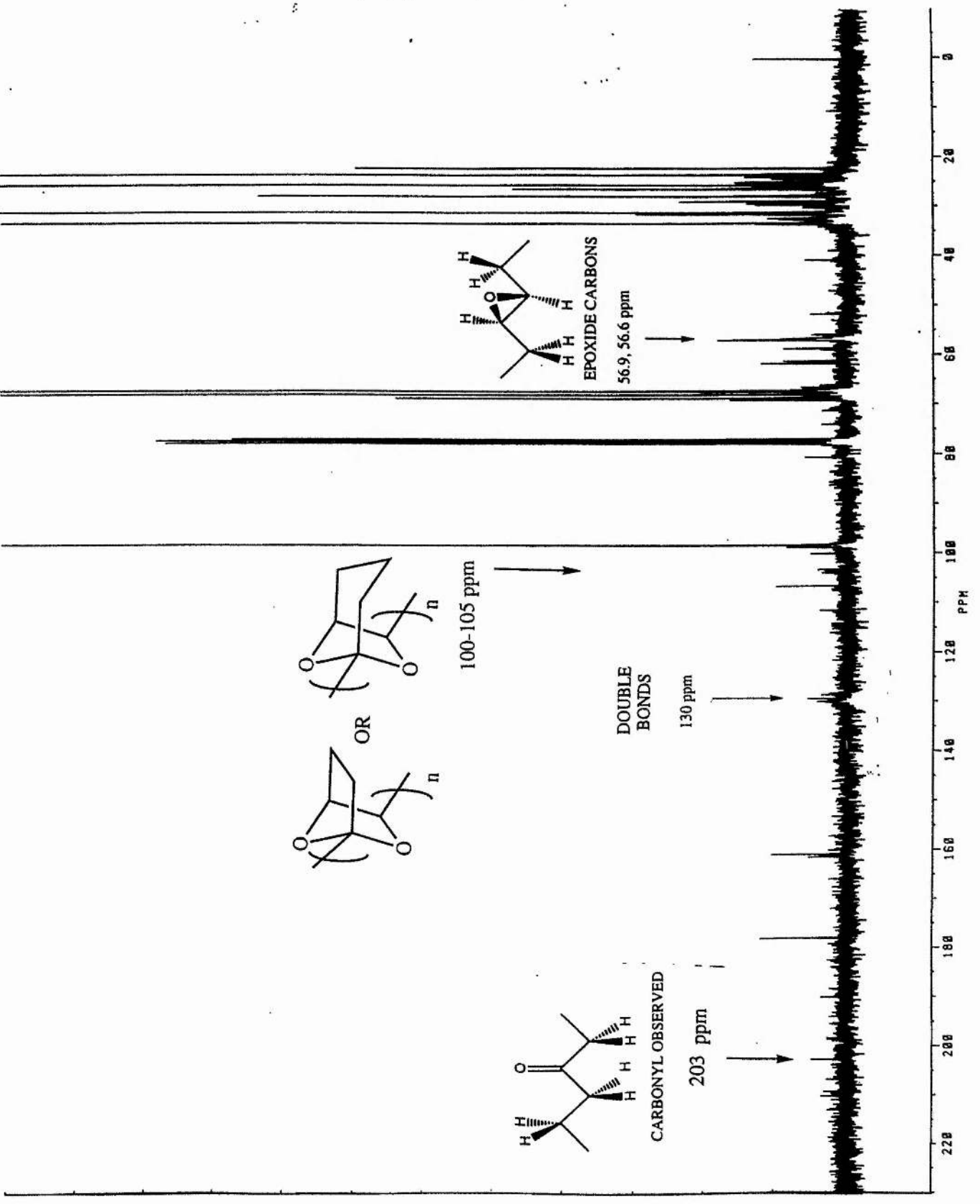
Solid Polyketone



Spectrum 3.11

Polyketone (LMWT-*cis*-PBD) - ^{13}C NMR

Isomerisation of polyepoxide (95%) with lithium bromide and THF.



3.3.3.7 MODEL REACTIONS

Model compounds with a structure similar to that of the polymer were used to study the isomerisation reaction. Initially, the model reaction were carried out using cyclododecatriene (figure 3.8) which involved epoxidation followed isomerisation.

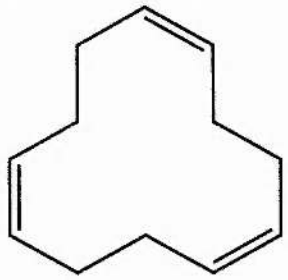


Figure 3.8: Cyclododecatriene

The ratio of the cyclododecatriene to the amount of lithium bromide was varied, table 3.6. Little evidence for epoxide or ketone formation was observed, therefore, an alternative substrate 2,3-epoxybutane was investigated.

TABLE 3.6

TABLE OF RATIOS FOR LITHIUM BROMIDE TO SUBSTRATE

ISOMERISATION REACTION	RATIO OF LiBr:CYCLODODECATRIENE
1	1 : 10
2	2 : 1
3	1 : 1

3.3.3.7.1 ISOMERISATION OF 2,3-EPOXYBUTANE

2,3-epoxybutane (figure 3.9) is similar in structure to the polybutadiene epoxide and to those molecules studied by Rickborn and Gerkin, and allows a direct study of the isomerisation reaction.

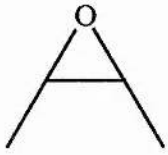


Figure 3.9: 2,3-epoxybutane

Two methods of epoxide-carbonyl rearrangement described by Rickborn and Gerkin[96] were used to investigate the isomerisation of 2,3-epoxybutane. Method one entails the addition of a homogeneous LiBr/HMPA solution to the epoxide and the other involves sequential addition of HMPA and LiBr to the epoxide. Rickborn and Gerkin found that 2,3-epoxypentane similar to 2,3-epoxybutane was readily converted to equal amounts of pentan-3-one and pentan-2-one.

METHOD ONE:

Isomerisation of an epoxide to a ketone using a homogeneous lithium bromide and HMPA solution.

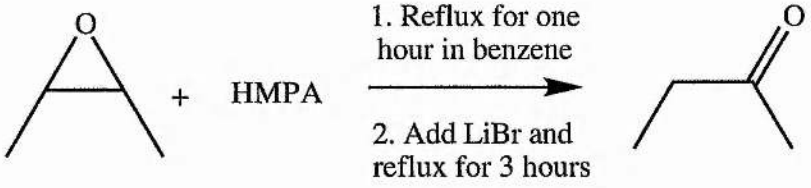
The lithium bromide was prepared by adding it to a predried Schlenk tube and heating it under vacuum to remove any water present. The solvent, in this case benzene, was then added to the lithium bromide before the addition of HMPA. The solution was allowed to stir until the lithium bromide had completely dissolved before the 2,3-epoxybutane was added.

Analysis by NMR and FTIR showed no evidence for the conversion of the epoxide to the ketone for either compound, indicating that this method of isomerisation was unsuccessful.

METHOD TWO:

Isomerisation of an epoxide to a ketone with sequential addition of lithium bromide and HMPA.

A solution of the 2,3-epoxybutane in benzene was prepared. To this was added the HMPA and the resulting solution was allowed to reflux for one hour before the lithium bromide was added, Equation 3.6.



Equation 3.6: Lithium bromide catalysed isomerisation of 2,3-epoxybutane in benzene with HMPA as the solubiliser. (HMPA and LiBr added sequentially.)

This method of isomerisation was successful in converting the 2,3-epoxybutane to butan-2-one in a 95% yield (see spectra 3.12 and 3.13 on page 125 and 126.)

3.3.3.7.2 EFFECT OF REACTION SOLVENT AND SOLUBILISING AGENT ON THE SOLUBILITY OF THE EPOXIDE

These model epoxidation studies were then used to investigate the effects of different solubilising agents on the epoxide-ketone isomerisation reaction.

TABLE 3.7

TABLE OF COMPONENTS USED IN EACH MODEL ISOMERISATION REACTION

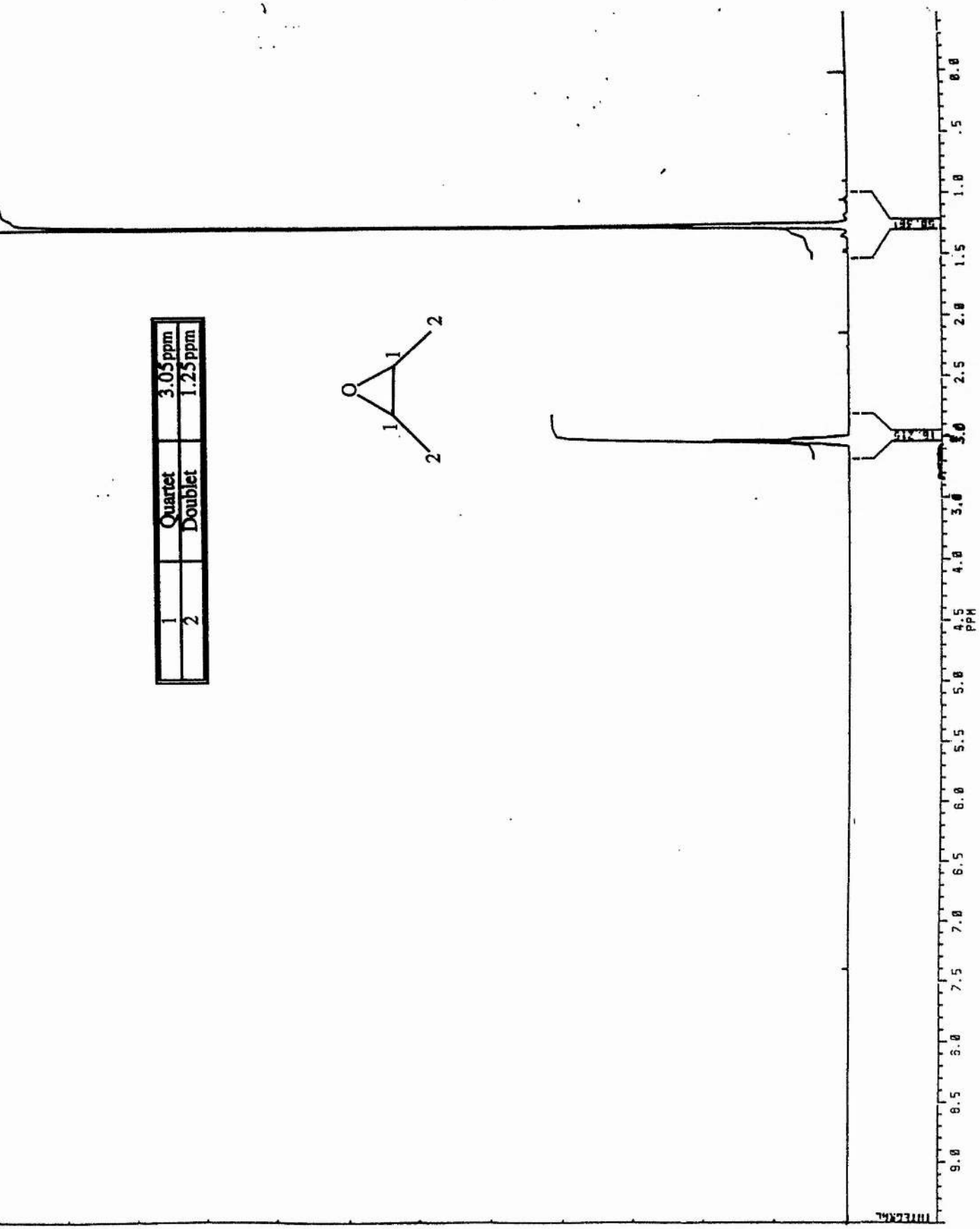
REACTION NUMBER	STARTING MATERIAL	SOLUBILISING AGENT	SOLVENT
1	2,3-epoxybutane	HMPA	Benzene
2	2,3-epoxybutane	DMI	Benzene
3	2,3-epoxybutane	DMPU	Benzene

NMR analysis indicated that LiBr/dimethyl imidazolidinone in one hour had converted 2,3-epoxybutane to butan-2-one in a >95% yield whereas LiBr/hexamethylphosphoramide gave only a 40% yield under the same conditions. Dimethylpropene urea on the other hand either delayed or prevented the reaction, as no conversion of 2,3-epoxybutane was observed. The rate of the reaction has increased as a result of changing the solubilising agent from HMPA to DMI, allowing essentially complete conversion to the ketone in one hour using DMI compared to three hours for HMPA. Complete conversion of the epoxide to the ketone is shown by comparing the ^1H NMR spectra of 2,3-epoxybutane and the product butan-2-one in which a characteristic doublet at 1.8 ppm and quartet at 3.0 ppm for the 2,3-epoxybutane are observed in the starting material (spectrum 3.12 on page 125) and a characteristic triplet at 0.9 ppm, singlet at 1.8 ppm and quartet at 2.1 ppm for butan-2-one are observed in the product (spectrum 3.13 on page 126). The characteristic resonances for 2,3-epoxybutane are absent in the product indicating that the reaction has gone to completion.

Spectrum 3.12

^{1}H NMR

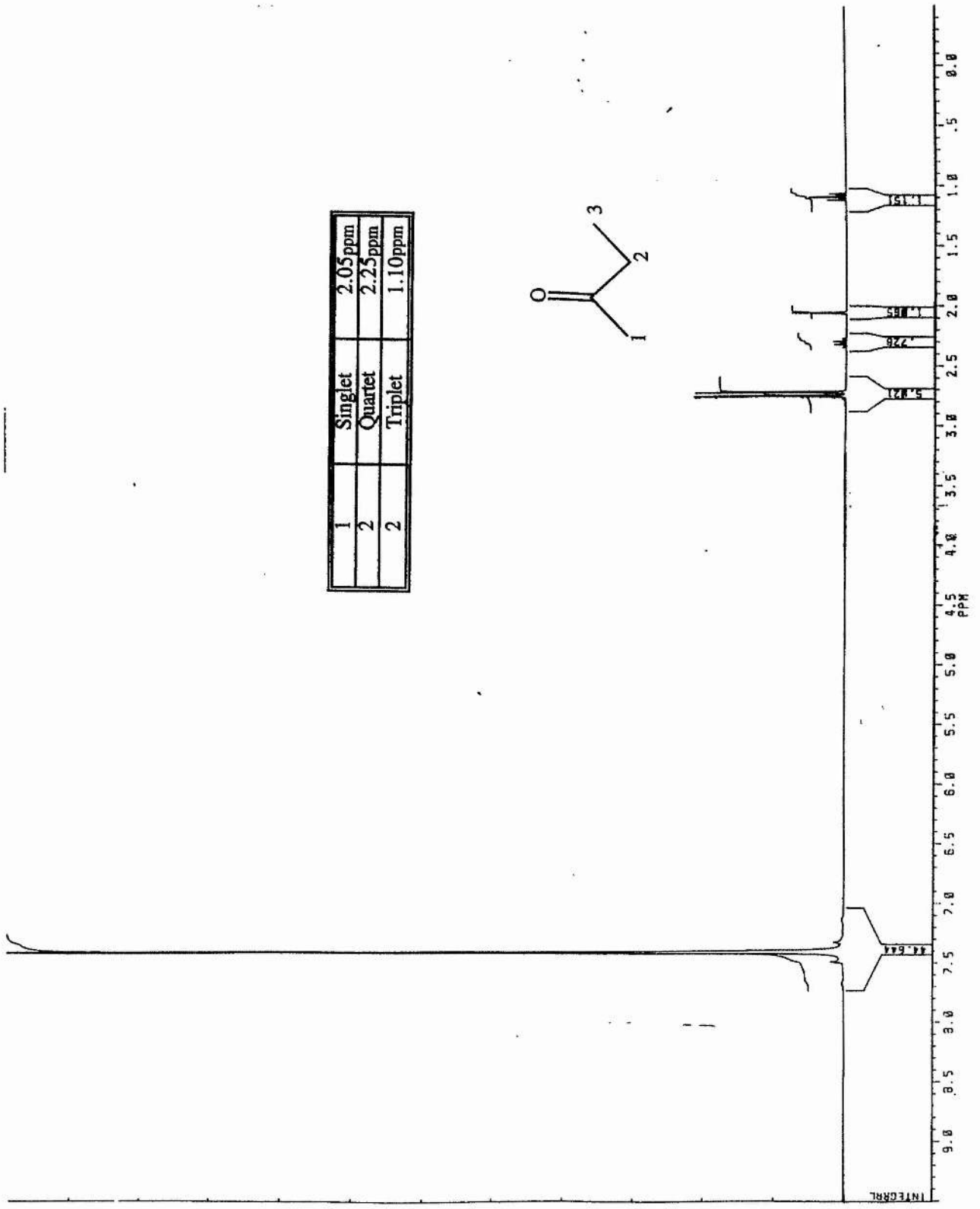
2,3-epoxybutane



Spectrum 3.13

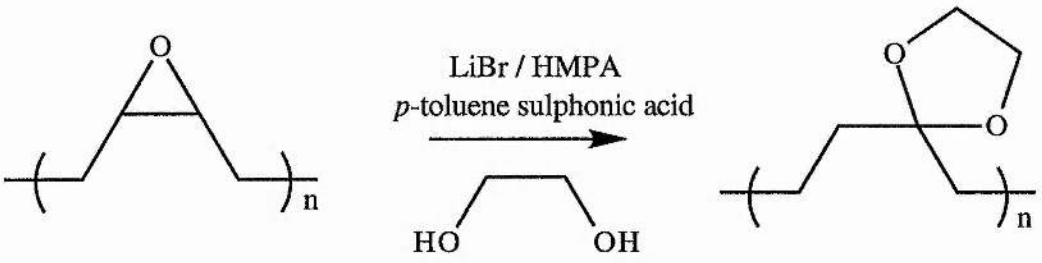
^{1}H NMR

butan-2-one



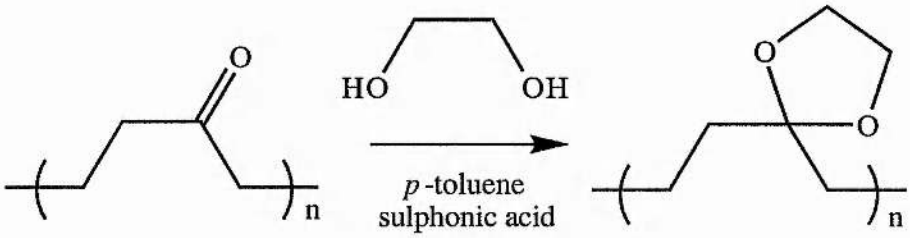
3.3.3.8 DERIVATISATION OF THE POLYBUTADIENE KETONE

Ethylene glycol in the presence of *p*-toluene sulphonic acid is reported to convert ethene-carbon monoxide copolymer to the more soluble alkene-dioxolane copolymer.[97] Therefore, the solubility problem encountered with the polyketones may be overcome by introducing ethylene glycol and *p*-toluene sulphonic acid into the reaction, and as each carbonyl group is formed it will be converted to the acetal, Equation 3.7.



Equation 3.7: IN SITU Derivatisation of the polyketone to the acetal formed from the polyepoxide

Addition of the ethylene glycol to the above reaction inhibited the conversion of epoxide groups, due to the complexing of lithium with the ethylene glycol. To avoid this interaction polyketones were prepared before the addition of the ethylene glycol, Equation 3.8.



Equation 3.8: Derivatisation of the polyketone to the acetal after isomerisation of the polyepoxide

In each reaction a solid lump was obtained, therefore, no reaction with the ethylene glycol was observed as the solid polyketones would not disperse. Low molecular weight polybutadiene was epoxidised and isomerised in an attempt to obtain a dispersed polyketone, however, only solid products were obtained.

3.3.3.9 ISOMERISATION OF POLYBUTADIENE EPOXIDE USING METHOD 2

Isomerisation of polyisoprene epoxides (see later) using method 2 (see page 123) showed by the ^{13}C NMR consistent formation of carbonyl groups. Therefore, the LMWT-*cis*-polybutadiene epoxides were isomerised using the same method in anticipation that this would result in carbonyl formation. The percentage conversion to the polybutadiene epoxide of up to 95% was obtained for the polyepoxide formed in dichloromethane with molecular sieves.

In each epoxidation reaction no unreacted double bonds were observed, indicating that all the back-bone double bonds had reacted to give either diol or epoxide.

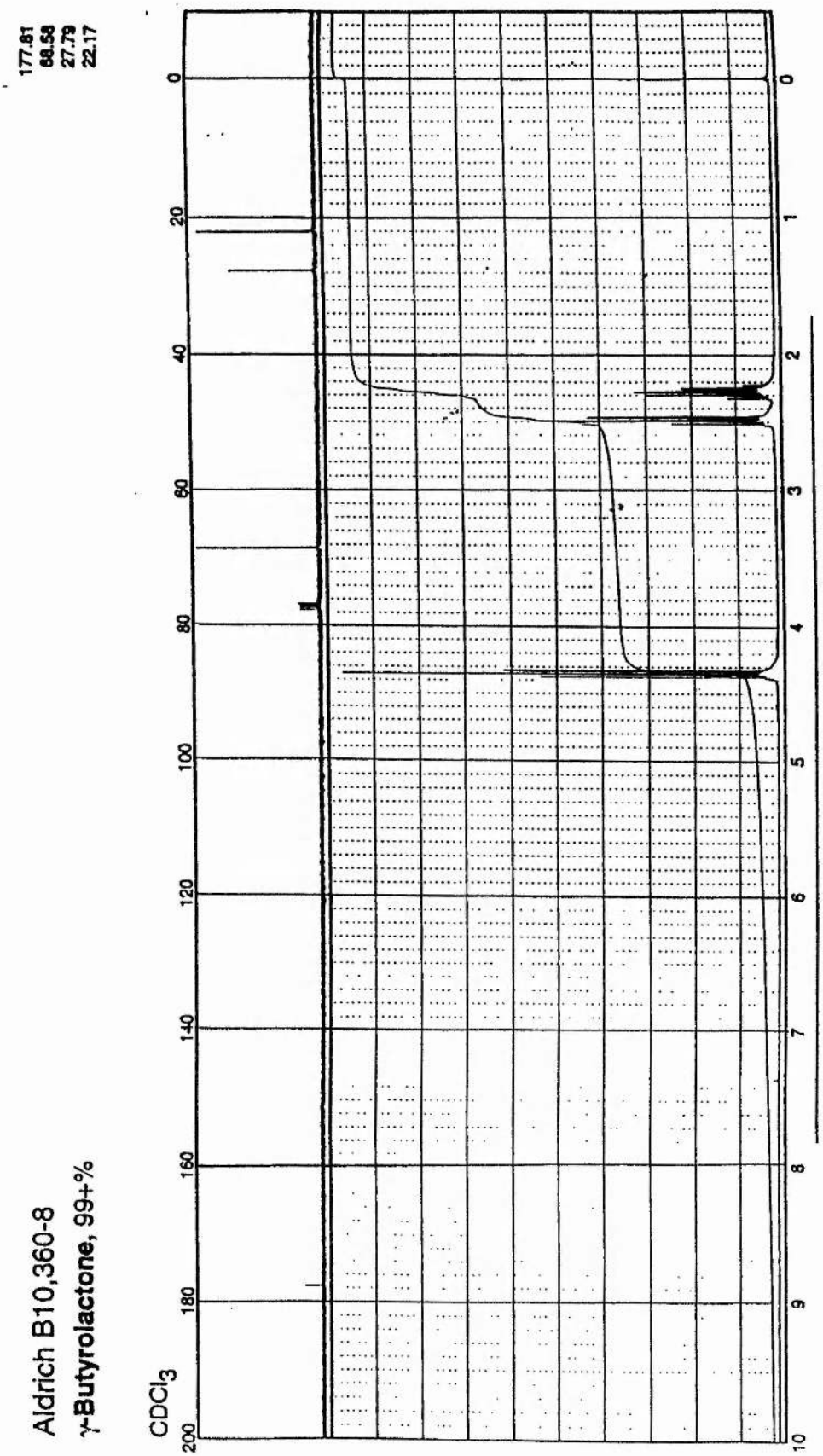
The subsequent isomerisation of the polyepoxide samples involved the addition of HMPA to the polymer solution in THF followed by lithium bromide. Analysis of the reaction products by ^{13}C NMR showed no presence of carbonyl resonances indicating the absence of ketone functionalities in the polymer backbone. However, resonances between 100 and 105 ppm were observed, which may be due to the presence of characteristic brevicomin type moeties as discussed earlier, would indicate intermediate ketone formation, see pages 118-9.

The THF solutions obtained from the isomerisation reactions also showed characteristic bands for butyrolactone at 178 ppm in the ^{13}C NMR spectra. To confirm the oxidation of THF, the remaining THF in one solution was removed leaving a residue of the polymer and other reactants. This residue produced strong signals for butyrolactone at 2.3, 2.5 and 4.3 ppm in the ^{1}H NMR spectra confirming the oxidation of THF, see spectrum 3.14 (butyrolactone) and 3.15 (residue from isomerisation reaction), page 129 and 130. No characteristic resonances from the polymer were observed in this spectrum indicating that the polymer was a solid which was stuck to the bottom of the flask.

Spectrum 3.14

^{1}H NMR and ^{13}C NMR

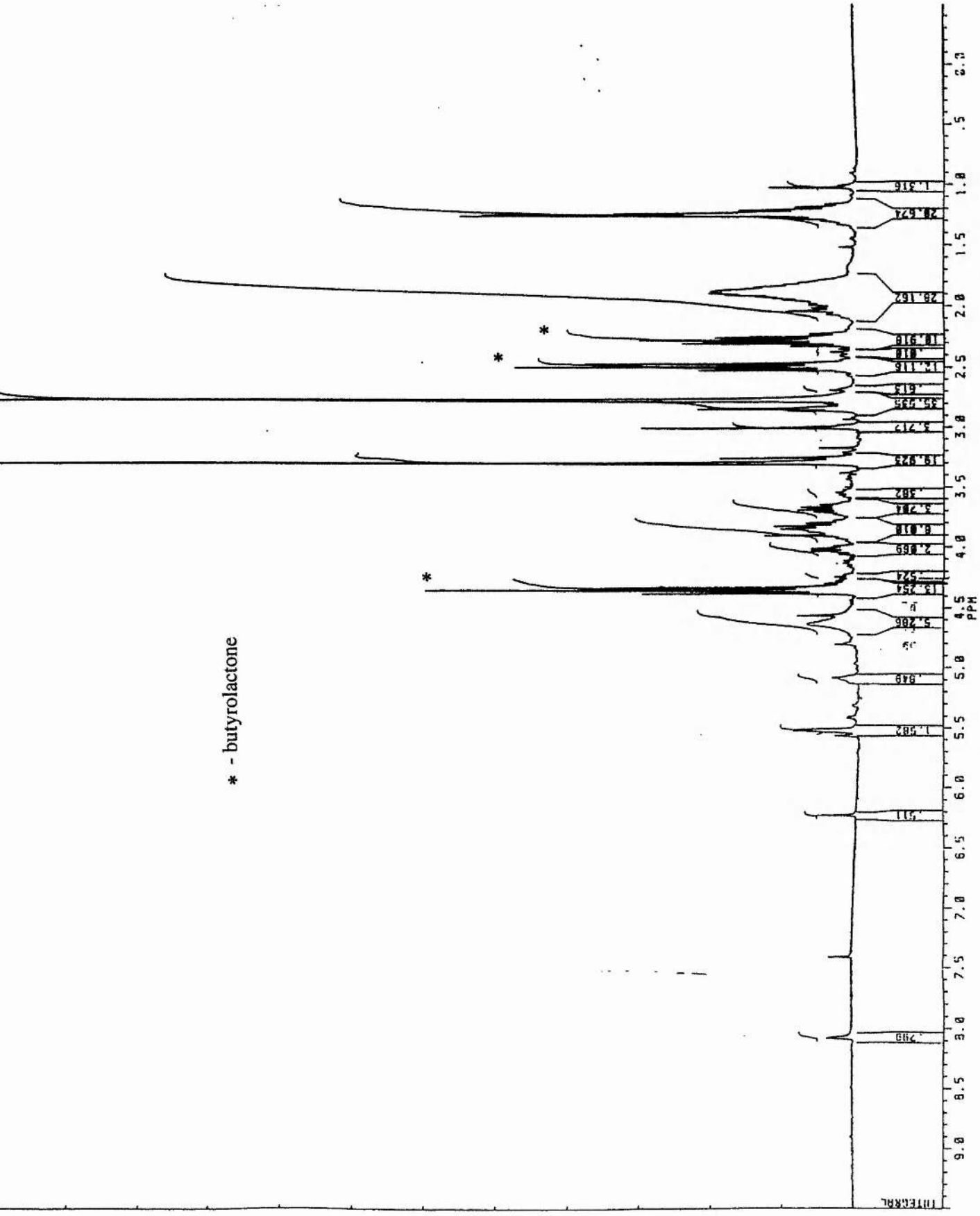
Butyrolactone



Spectrum 3.15

Polyketone - ^{1}H NMR

Residue from polyepoxide isomerisation.



3.3.3.10 CONCLUSIONS - THE INFLUENCE OF CHANGES IN SOLVENT, SOLUBILISING AGENT AND SUBSTRATE ON THE ISOMERISATION REACTION OF EPOXIDES

The polybutadiene epoxide substrate used in the isomerisation reaction was obtained in high conversions (>95%) using Bu^tOOH catalysed by [MoO_2Cl_2(diethoxyphosphoryl camphor)] in the presence of molecular sieves. The isomerisation of the polybutadiene epoxide gives rise to polyketones which are white solids insoluble in common organic solvents including m-cresol and hexafluoroisopropanol. This is also the case for the ethene-carbon monoxide copolymer although it is soluble in hexafluoroisopropanol and m-cresol. The polybutadiene ketone, however, does exhibit swelling in some solvents indicating the possibility of crosslinking, which may account for its insolubility in hexafluoroisopropanol and m-cresol.

The main problem with the polybutadiene ketone has been the insolubility of the product, making characterisation and purification of the material difficult, although a characteristic carbonyl band in the infrared at 1710 cm^{-1} has been observed along with a characteristic carbonyl resonance at 210 ppm in the ^{13}C solid state NMR indicating the formation of ketone function in the polymer chain.

The insolubility of the polyketone product is important and as a result has been investigated via changes in reactants such as substrate, solubilising agent and reaction solvent, and also via derivatisation of the polyketone to form a more soluble polydioxolane.

Initially, the molecular weight of the polybutadiene was reduced to make the removal of molecular sieves in the epoxidation reactions easier and secondly to improve the accessability of the lithium for coordination to the epoxide in the isomerisation reactions. It was thought that if a small degree of crosslinking had occurred in the high molecular weight polymer (2-3,000,000) then it would have become insoluble due to the large change in molecular weight, therefore, a lower molecular weight polymer (2-300,000) was utilised as this would not experience such a dramatic change in molecular weight and consequently reduce the chance of insolubility through crosslinking.

As a result the easy removal of molecular sieves from the LMWT-polybutadiene epoxide solution was achieved and also gave rise to a less viscous solution which was easier to remove via catheter. Although the change in molecular weight of the polybutadiene allowed the easy removal of molecular sieves and reduced the viscosity of the polyepoxide solution, it did not solve the problem of the insoluble polyketone.

Other factors were studied, firstly was the ratio of lithium bromide to polybutadiene epoxide, which has been shown to be significant in the conversion of epoxide to ketone. In generally the higher the level of lithium bromide the greater the conversion of epoxides, until a stoichiometric amount was used which gave complete conversion; consequently additional lithium bromide had no effect. The fact that stoichiometric amounts of lithium bromide are

required to give complete conversion of the epoxide indicates that the reaction is not catalytic, although this observation may be the result of lithium being bound within the polymer and therefore not available to continue the ring opening reaction.

Secondly, when the HMPA (solubiliser) was removed from the isomerisation reactions it was suggested that the lithium cation was chelating to the polymer as partial solubility of the lithium bromide was observed which resulted in the formation of carbonyl groups detected in the infrared spectra at 1710 cm^{-1}. The interaction between the polyketone and lithium was confirmed by a model reaction in which the carbonyl resonance of 2,5-hexandione shifts from 207.5ppm to 208 ppm when lithium bromide is added.

Model reactions with 2,3-epoxybutane were used to investigate alternative solubilising agents, such as dimethyl imidazolidinone (DMI) and dimethylpropylene urea (DMPU) as removal of the lithium bromide in reactions without such an agent proved difficult. The reactions indicated that DMPU was unsuccessful in assisting the isomerisation as no butan-2-one was observed, however, DMI was more as effective than HMPA in converting the epoxide to the ketone and had the advantage of being less toxic and would therefore be a good substitute for HMPA. Consequently, isomerisation reactions involving polybutadiene epoxide were carried out using DMI as the solubilising agent. The NMR analysis of these reaction solutions did not indicate the presence of carbonyl groups, although they were observed in the infrared spectra of the solid products, indicating the presence of ketonic functionalities, however, the problem with insoluble products has not been resolved.

A possible solution to this is the derivatisation of the polyketone to a more soluble dioxolane polymer[97] using ethylene glycol and *p*-toluene sulphonic acid as shown for the ethene-carbon monoxide copolymer. Unfortunately, the dioxolane polymer was not obtained as the polyketone formed would not dissolve or disperse in solution. Ethylene glycol and *p*-toluene sulphonic acid were added to the polyepoxide in the isomerisation reaction in an attempt to convert each individual carbonyl group as it is formed to the dioxolane avoiding the insoluble polyketone. No change in the polybutadiene epoxide was observed suggesting that the ethylene glycol interacted with the lithium bromide thus preventing any reaction.

We can conclude that the lithium salt catalysed isomerisation of the polybutadiene epoxide to the polybutadiene ketone would appear to be successful, as qualitative analysis of the solid polybutadiene ketone by NMR and FTIR have indicated the presence of carbonyl groups in the polymer backbone, the disappearance of epoxide groups previously formed and the complete conversion of the double bonds available in the polybutadiene.

The infrared spectra of the solid products show a characteristic carbonyl band at 1710 cm^{-1} indicating the presence of ketonic functionalities. This conclusion is supported by the observed characteristic carbonyl resonance in the solid state NMR spectrum at 210 ppm. Both spectra also indicate that all the epoxide groups previously formed in the polymer backbone have reacted as no characteristic resonances appear at ~56 ppm in the ^{13}C NMR or at 905 and 965 cm^{-1} in the IR. The ^{13}C NMR also indicated the presence of unreacted double bond in the

final polymer, however, analysis of the substrate polyepoxide indicates that they are not from unreacted double bonds but may have arisen from crosslinking via aldol condensation reactions, which may explain the low solubility of the product.

In addition, promising results obtained by infra red and NMR spectroscopy of reactions with no solubilising agent indicated that soluble polyketones can be prepared successfully via the isomerisation of polyepoxides using only the lithium salt in THF. In the ^{13}C NMR a characteristic carbonyl resonance at 203 ppm and a resonance for unreacted epoxide groups at 56 ppm are observed. They were also resonances due to brevicomin type moeties[99] between 100 and 105 ppm (assuming they are not due to impurities), indicating that the soluble polymer contains not only ketone and epoxide groups but also cyclic ketal structures, formed from the reaction of an epoxide with a neighbouring ketone.[100]

3.4. POLYISOPRENE

After initial isomerisation reactions with polybutadiene epoxide it was identified that the solubility of the resultant polyketone was a major concern. Therefore, the investigation into the solubility of the polyketone formed also encompassed a study of the isomerisation of the polyisoprene epoxide as polyisoprene, unlike polybutadiene, has a tertiary carbon atom at the double bond in the polymer backbone (figure 3.10) and when epoxidised it leaves only one available site (carbon) at the double bond for the formation of carbonyl group.

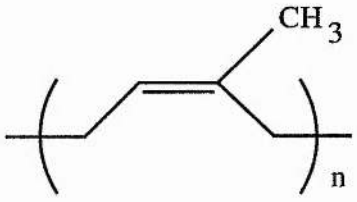


Figure 3.10: The microstructure of polyisoprene
in which there is a tertiary carbon atom.

Since a methyl shift is energetically unfavourable in this reaction, the tertiary carbon atom will force the carbonyl group onto the opposite end of the double bond as a pentavalent carbon atom cannot exist, hence creating a more regular position of the carbonyl group, as shown in the figure below.

Figure 3.11: Polyketone possibly from polyisoprene epoxide.

This produced a regular polyketone with pendant methyl groups and an additional carbon atom between the carbonyl groups compared to the ethene-carbon monoxide copolymer which has only two carbon atoms between each carbonyl group. The additional carbon atom in the polyisoprene may disrupt the packing of the polymer chain due to the increase in the degrees of freedom of rotation, reducing crystallinity and consequently the melting point of the polyketone.

It is therefore of interest to study the isomerisation of the polyisoprene epoxide to examine the effect of this microstructure on the solubility of the resultant polyketone.

3.4.1 INITIAL ISOMERISATION REACTION OF POLYISOPRENE IN THF

Epoxidation reactions of polyisoprene were carried out in tetrahydrofuran (THF) as this dissolved the polyisoprene more readily than any other solvent. Unfortunately, the percentage conversion to epoxide and/or diol could not be determined because the region in the ^{1}H NMR where the diols peaks are expected was masked by signals from THF. Without knowing the amount of diol produced it was difficult to assess the amount of epoxide present although characteristic epoxide resonances were observed at 60 ppm and 64 ppm in the ^{13}C NMR spectra. In addition, no characteristic diol resonance was observed at 82 ppm in the ^{13}C NMR. Consequently, the isomerisation reaction involving polyisoprene epoxides were carried out in THF. The result of are show in table 3.8.

TABLE 3.8

THE EPOXIDATION AND ISOMERISATION OF POLYISOPRENE

		% CONVERSION FOR EPOXID[n] RXNS			ISOMERISATION RXN	
RXN	SOLVENT	EPOXIDE *cis*	DIOL	UNREACTED DOUBLE BONDS *cis*	ISOMER[n] to KETONE	DOUBLE BONDS
1	THF	epoxide observed	not observed due to THF	NONE	^{13}C res at 178, 202, 203ppm	^{13}C res at 130 ppm
2	THF	epoxide observed	not observed due to THF	NONE	^{13}C res at 202, 203ppm	^{13}C res at 130 ppm

a - Starting material was polyisoprene with 99% *cis* double bonds
(M.W. = 2-3,000,000)

In each reaction the lithium bromide was added to the polymer solution followed by the solubilising agent and the resultant mixture was refluxed for fifteen minutes.

The soluble products from these reactions were analysed using NMR spectroscopy and were shown to exhibit characteristic resonances for carbonyl formation at 203 and 204ppm in the ^{13}C NMR. There are no characteristic double bond resonances at 5.5ppm in the ^{1}H NMR and 125 and 135ppm in the ^{13}C NMR. (see spectra 3.16, 3.17, 3.18 and 3.19 on pages 137-140). Characteristic resonances for the epoxide are still present, indicating that not all of the epoxide groups have been converted to ketonic groups. However, other carbon double bond resonances are observed at 130ppm but they are probably due to crosslinking via aldol type reactions.

Other resonances at 2.3, 2.5 and 4.3 ppm in the ^{1}H NMR spectra and at 22, 27.8, 68.6 ppm and 177.8 ppm in the ^{13}C NMR spectra indicate the presence of butyrolactone from the oxidation of tetrahydrofuran by residual $Bu^{t}OOH$ from the epoxidation reaction as an excess was used. Also observed were resonances between 100 and 105 ppm for which there are two explanations as discussed earlier, either the presence of impurities or the formation of brevicomin type moeties in the polymer chain via reaction of ketonic groups with nearby epoxides.

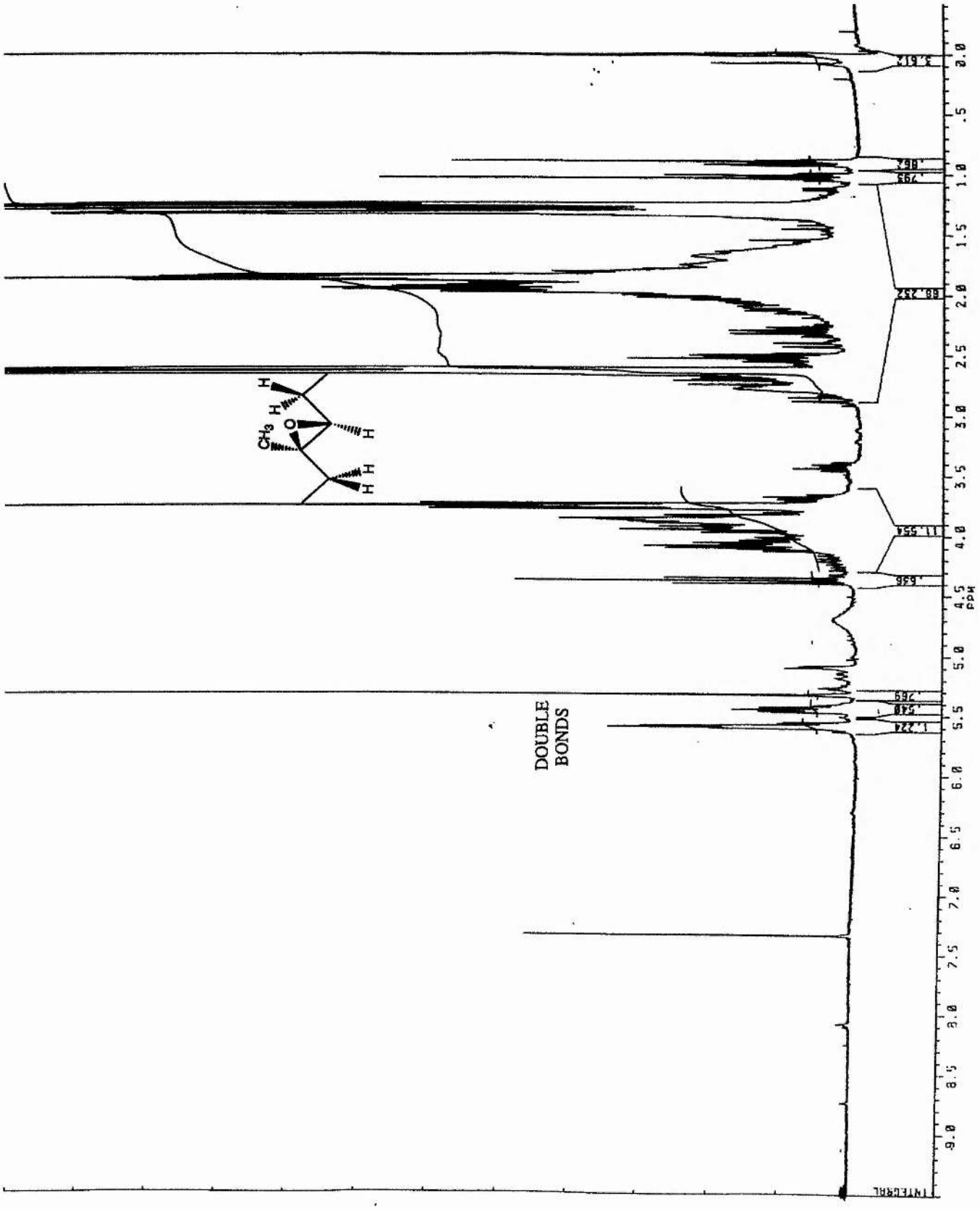
These encouraging NMR results confirmed that reactions involving lithium bromide isomerisation of polyisoprene epoxide were successful in preparing soluble polymers with carbonyl, epoxide and possibly ketal groups, which can be analysed by solution NMR.

The formation of carbonyl groups in the soluble polymers is supported by FTIR studies in which a characteristic carbonyl band is observed at 1710 cm^{-1}, spectrum 3.20 on page 141.

Spectrum 3.16

Polyketone (LMWT-PISOP) - ^{1}H NMR

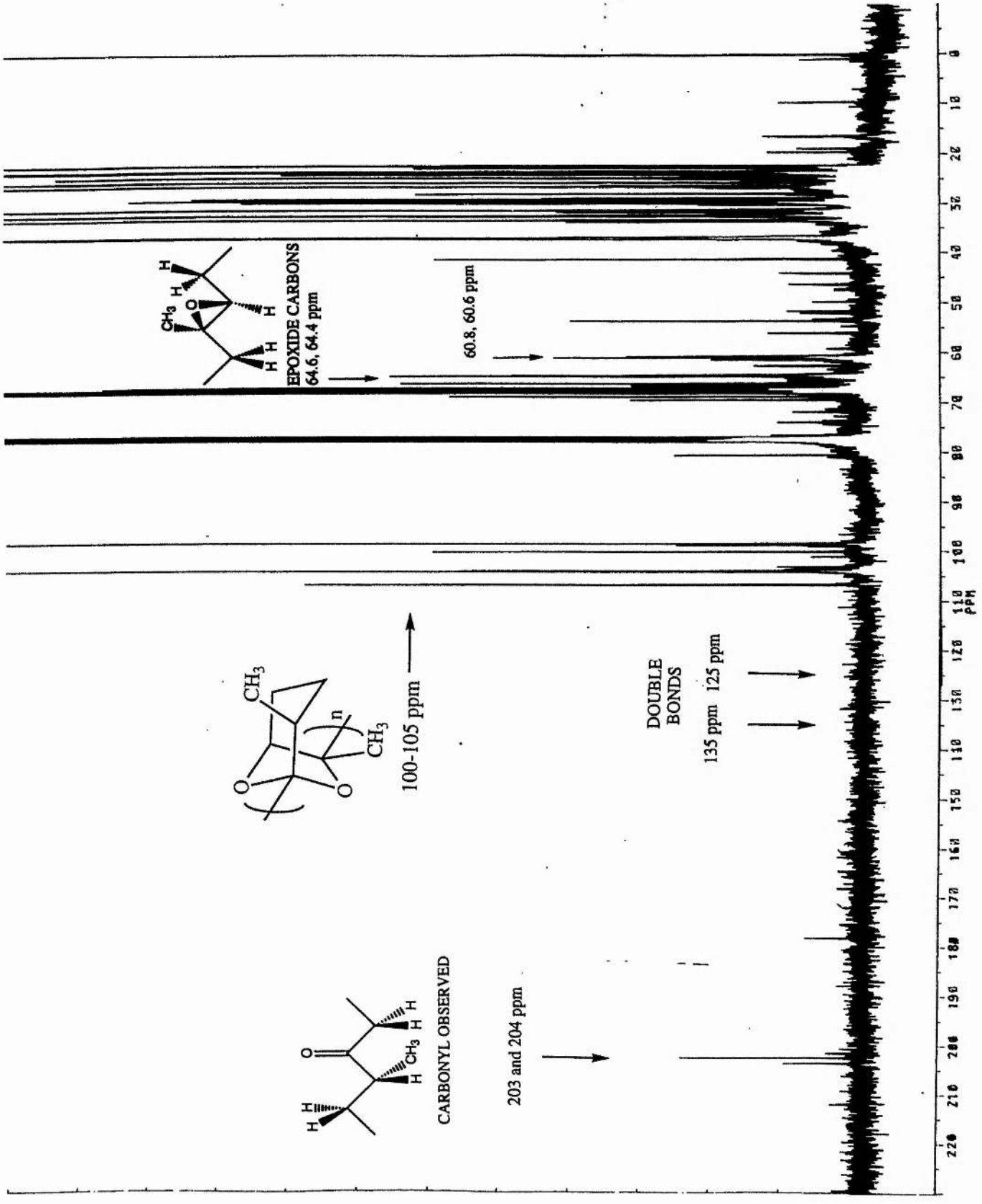
with molecular sieves



Spectrum 3.17

Polyketone (LMWT-PISOP) - ^{13}C NMR

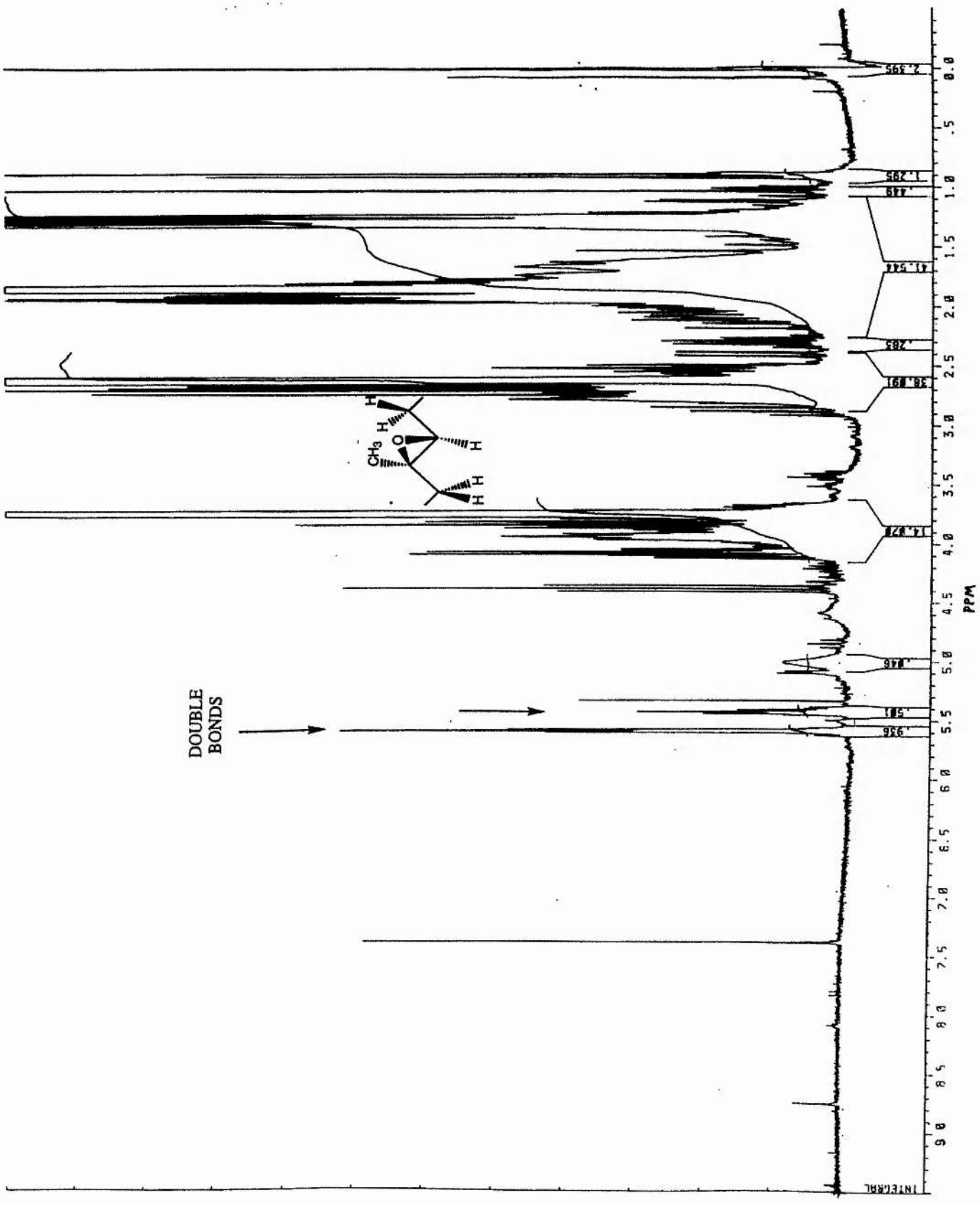
with molecular sieves



Spectrum 3.18

Polyketone (LMWT-PISOP) - ^{1}H NMR

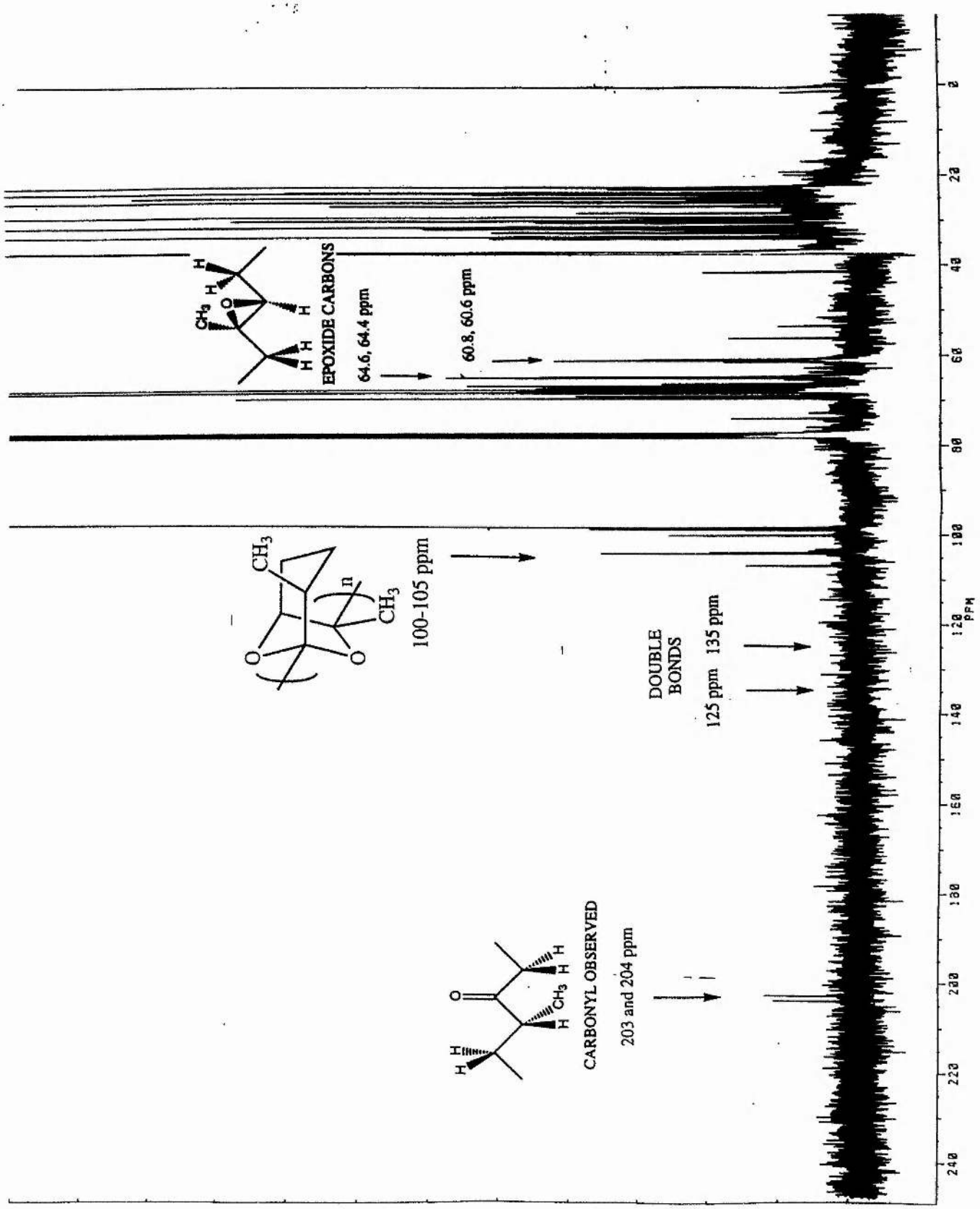
with molecular sieves



Spectrum 3.19

Polyketone (LMWT-PISOP) - ^{13}C NMR

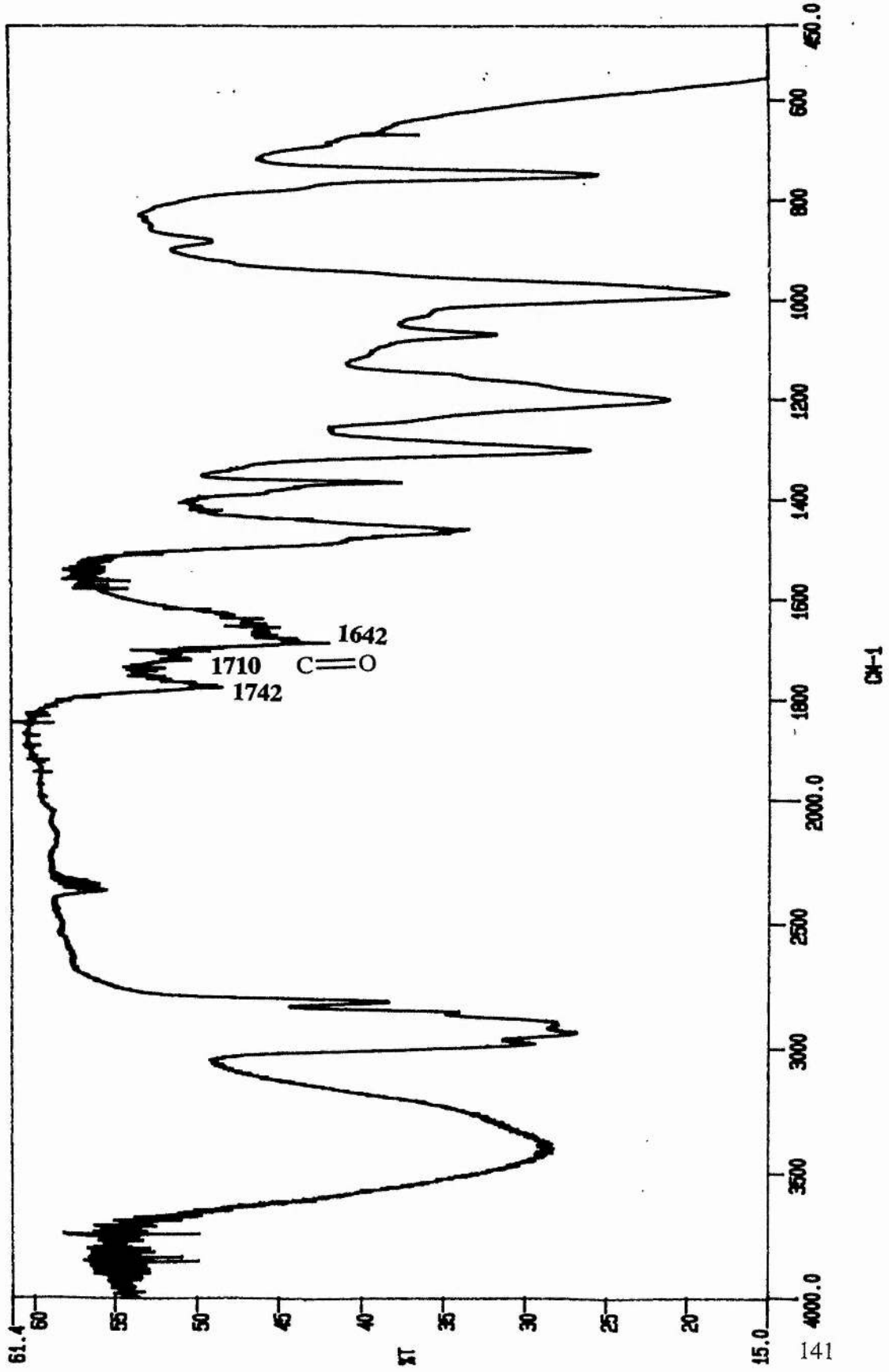
with molecular sieves



Spectrum 3.20

Polyketone (LMWT-PISOP) - FTIR

with molecular sieves



3.4.2 POLYISOPRENE EPOXIDE ISOMERISATION REACTIONS IN THF AND CH_2Cl_2

Problems previously encountered with the measurement of epoxide/diol conversions (i.e. the masking of the diol by THF) resulted in the use of dichloromethane as a solvent for the epoxidation of polyisoprene. Consequently, a series of isomerisation reaction involving polyisoprene epoxide reactions were investigated in two solvents, THF and CH_2Cl_2, to gain a comparison between the polyketone products obtained for each solvent system. The polyisoprene epoxides were prepared in the presence of molecular sieves to remove adventitious water from the system preventing the deactivation of the molybdenum catalyst. Samples prepared in THF show characteristic epoxide resonances (table 3.9) but the amount of diol is not known due to the masking of the diol resonances by the THF in the ^1H NMR.

TABLE 3.9

CONVERSION OF POLYISOPRENE EPOXIDE TO KETONE

	SOLVENT	% CONVERSION FOR EPOXID^n RXNS			ISOMERISATION RXN	
RXN b	/SOL AGENT	EPOXIDE	DIOL	DOUBLE BOND	KETONE	DOUBLE BONDS
1a	THF /DMI	epoxide observed	not observed due to THF	NONE	carbonyls observed	^{13}C res at 130 ppm
2a	THF /DMI	epoxide observed	not observed due to THF	NONE	carbonyls observed	^{13}C res at 130 ppm
3a	CH_2Cl_2 /DMI	>95	-	NONE	carbonyls observed	^{13}C res at 130 ppm
4a	CH_2Cl_2 /DMI	>80	-	NONE	carbonyls observed	^{13}C res at 130 ppm
5a	THF /DMI	epoxide observed	not observed due to THF	NONE	carbonyls observed	^{13}C res at 130 ppm
6a	THF /DMI	epoxide observed	not observed due to THF	NONE	carbonyls observed	^{13}C res at 130 ppm
7a	THF /DMI	epoxide observed	not observed due to THF	NONE	carbonyls observed	^{13}C res at 130 ppm
8a	THF /HMPA	epoxide observed	not observed due to THF	NONE	carbonyls observed	^{13}C res at 130 ppm
9a	THF /HMPA	epoxide observed	not observed due to THF	NONE	carbonyls observed	^{13}C res at 130 ppm
10a	THF /NONE	>95[c]	-	NONE	carbonyls observed	^{13}C res at 130 ppm
11a	THF /NONE	>95[c]	-	NONE	carbonyls observed	^{13}C res at 130 ppm

a - Polyisoprene with 99% *cis* double bonds (M.W. = 2-300,000)

b - All reaction were carried out in the presence of molecular sieves.

c - Epoxidation carried out in CH_2Cl_2.

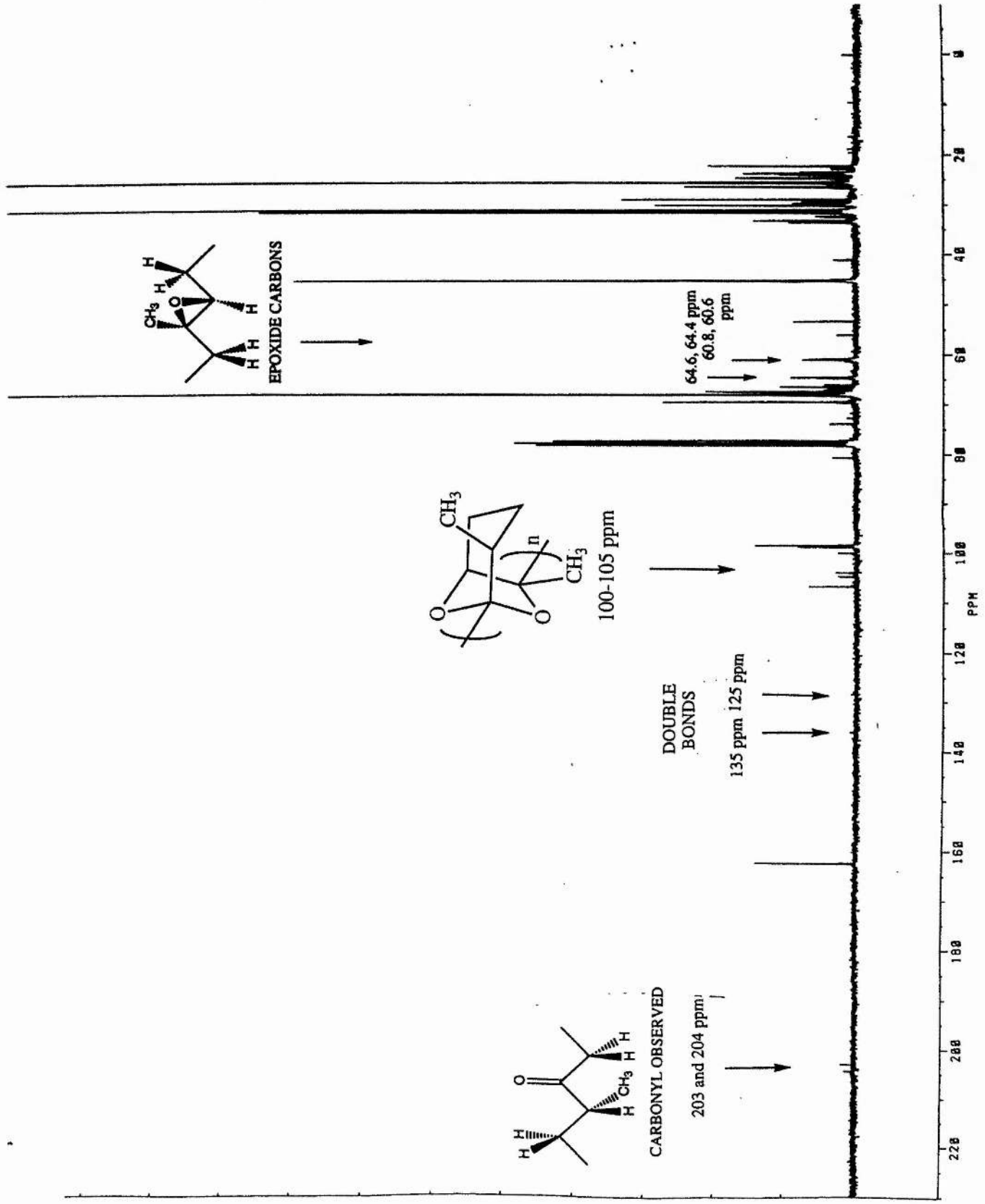
Using epoxidised polyisoprene as the substrate, a soluble product can be obtained by using HMPA or DMI in CH_2Cl_2 or THF or by using lithium bromide alone in THF. ^{13}C NMR studies of the crude reaction solution show the presence of two resonances at 203 and 204 ppm, characteristic of ketone units, although not all of the epoxide units have ring opened as indicated by residual resonances at 60 and 64 ppm, see ^{13}C NMR spectra 3.21 and 3.22 on pages 144 and 145. In addition, six resonances near 100 ppm, similar to those observed in the polybutadiene ketone, may have arisen from either impurities in the reaction solution or via reaction between ketone and neighbouring epoxide units to give brevicomin type structures along the polymer chain, as discussed earlier on page 118-9, although some of the resonances are attributed to other reactants, spectrum 3.23 on page 146.

Assuming the resonances between 100 and 105 ppm are due to the polymer and not impurities, this would explain the observation of low conversions to the ketone.

In the early stages of the reaction the ring opening of the epoxide will be random, but later on some of the epoxide may become isolated between brevicomin units as in the case of the polybutadiene ketone. These epoxides will either be oxidised to the ketone or it may be too sterically hindered to be attacked, which would again account for the fact that very high conversions to the ketone have not been observed. Like the polybutadiene ketone, more than one resonance is observed for each type of unit (ketone, brevicomin and epoxide), again suggesting a complex microstructure for the polymer.

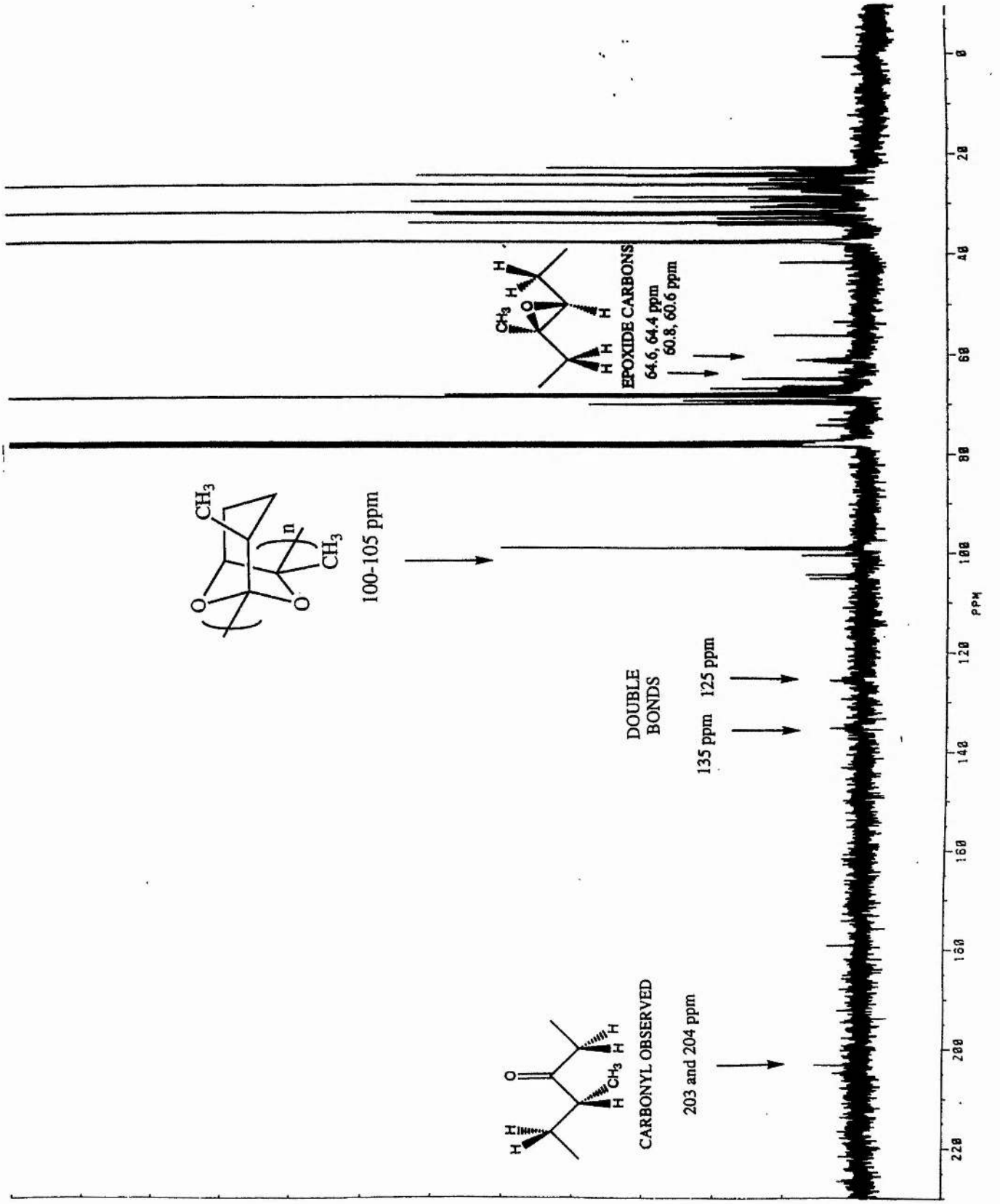
Spectrum 3.21

Polyketone (LMWT-PISOP) with DMI in THF - ^{13}C NMR



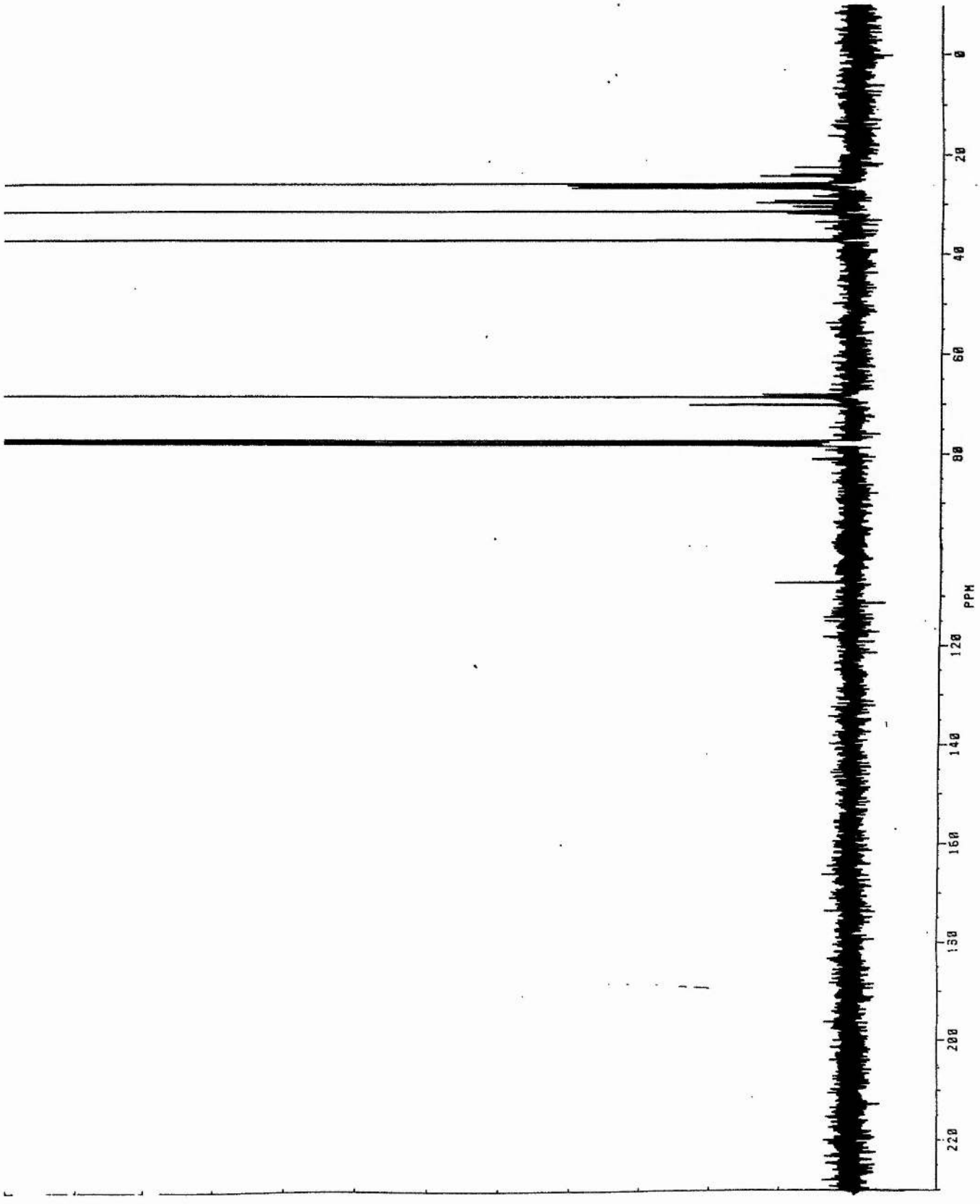
Spectrum 3.22

Polyketone (LMWT-PISOP) with HMPA in THF - ^{13}C NMR



Spectrum 3.23

Blank Reaction with HMPA in THF - ^{13}C NMR



3.4.3 CONCLUSIONS FROM THE POLYISOPRENE REACTIONS

Epoxidised polyisoprene produces soluble products when isomerised with lithium bromide using HMPA or DMI in CH_2Cl_2 or THF or by using lithium bromide alone in THF. ^{13}C NMR studies of the crude reaction solution show that characteristic ketone units have been formed but epoxide units still remain in the polymer. The spectra also shows the presence of ketal resonances attributed to brevicomin type moeties (assuming there are no impurities present) formed possibly from the reaction of an epoxide with a neighbouring ketone.

Therefore, the spectroscopic study by NMR has shown that the isomerised polyisoprene epoxides contain ketone, epoxide and possible ketal groups in the polymer backbone. The formation of these groups could involve random ring opening of the epoxide to form ketonic groups, some of which then react with neighbouring epoxides to form brevicomin type structures. Some epoxides will be isolated between brevicomin type units, as discussed earlier for polybutadiene ketone and they will either be oxidised to the ketone or may be too sterically hindered to be attacked. More than one resonance is observed for each type of unit (ketone, brevicomin and epoxide), suggesting a complex microstructure for the polymer.

CHAPTER FOUR

OXIDATION

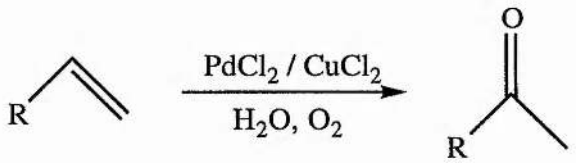
4.0 INTRODUCTION

4.1 OXIDATION OF POLYBUTADIENE

Oxidation of polybutadiene is of particular interest with the view of preparing a polyketone. There are many methods available for the oxidation of alkenes, alcohol and diols which may be studied in an attempt to prepare the polyketone. In this chapter, the oxidation methods studied have include the Wacker-type oxidation of polybutadiene to the ketone using $PdCl_2/CuCl_2$ or $RhCl_3.3H_2O$-$Cu(ClO_4)_2$ [101] with water, hydroboration-oxidation of polybutadiene followed by the oxidation of the secondary alcohol formed using $VO(acac)_2$-Bu^tOOH,[102] activated DMSO,[103] 4-methoxy-1-oxo-2,2,6,6-tetramethylpiperidinium chloride,[104-106] trichloromelamine[107] and the permanganate ion.[108]

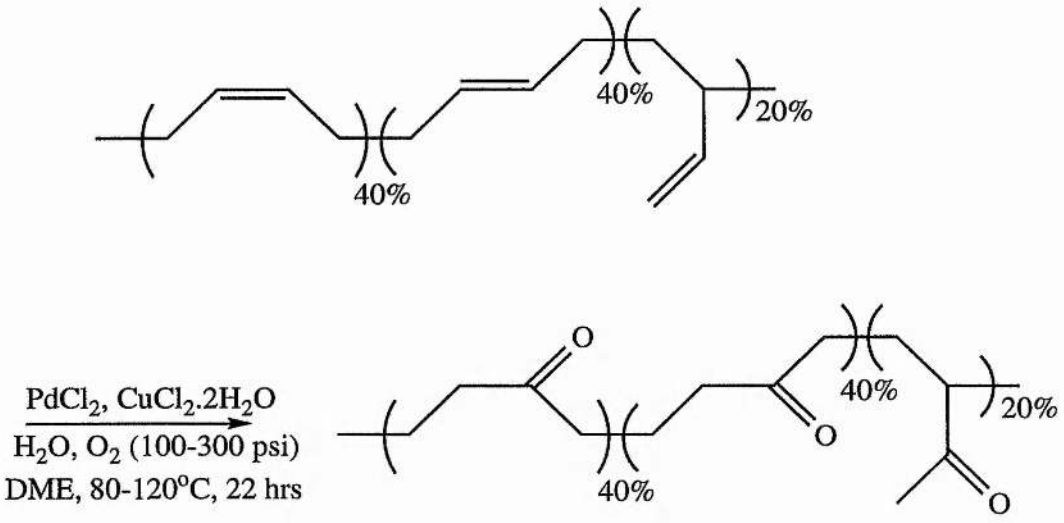
4.1.1 OXIDATION OF POLYBUTADIENE USING PALLADIUM CHLORIDE AND COPPER CHLORIDE

The oxidation of ethylene to acetaldehyde using $PdCl_2$ and $CuCl_2$ as catalysts under an oxygen atmosphere is well known as the Wacker process[109] (Equation 4.1), and is one of the most important processes employing transition metal catalysts.



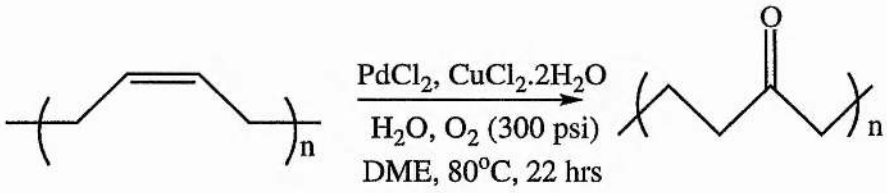
Equation 4.1: Oxidation of an alkene using palladium chloride and copper chloride in the presence of water under oxygen pressure.

The catalytic oxidation of polybutadiene using a Wacker type reaction has been recently reported.[68] This paper discusses the oxidation of 1,2-polybutadiene containing more than 90% vinyl pendant group, phenyl terminated polybutadiene containing 25% pendant double bonds and 40% *trans* backbone, and polybutadiene with 20% pendant vinyl groups and 80% *trans* and *cis* backbone double bonds. It was found that each polybutadiene, all of which contain pendant groups, can be converted to the polyketone using $PdCl_2$, $CuCl_2.2H_2O$ and H_2O (e.g. Equation 4.2). The oxidation was found to be sensitive to the reaction conditions, with high selectivity attained using 1,2-dimethoxymethane as the solvent at 80°C under an oxygen pressure of 300 psi for 22 hours.



Equation 4.2: Oxidation of polybutadienes with palladium chloride and copper chloride in the presence of water under oxygen pressure in DME.

This method was applied to the oxidation of 99% *cis*-1,4-polybutadiene in which a solution of the palladium chloride and the copper chloride was prepared in a 45 cm^3 autoclave to which was added a DME solution of the *cis*-1,4-polybutadiene and then finally water. The autoclave was purged with oxygen and pressurised to 300 psi, and heated to 80°C for 22 hours (Equation 4.3).

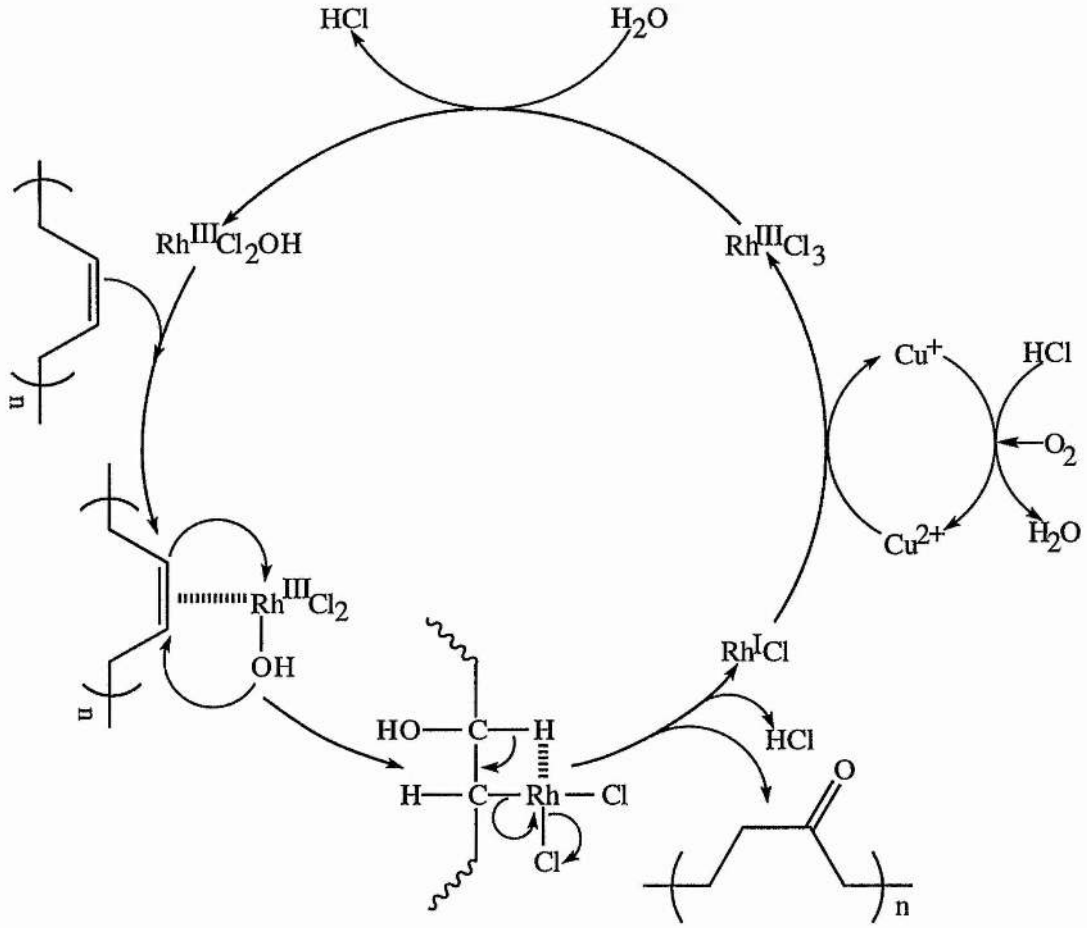


Equation 4.3: Oxidation of *cis*-1,4-polybutadiene using palladium chloride and copper chloride in the presence of water under oxygen pressure.

A solid product from the reaction was observed as the solution had been displaced during the reaction from the glass liner to the inside of the autoclave leaving behind the polymer and other reactants. Attempts to dissolve the polymer were futile, therefore analysis by nmr was not possible. Analysis to FTIR was not possible either as the product was very rubbery and of very low elasticity, consequently when stretched to obtain an FTIR the sample would rip. Future work is required to investigate the polymer concentration and the experimental procedure to ascertain if a soluble polyketone can be obtained from an all *cis*-polybutadiene by this method. Also of interest would be work involving polyisoprene to form the corresponding ketone to see if the methyl group influences the modification of the polymer.

4.1.2 CATALYTIC OXIDATION OF POLYBUTADIENE WITH $[RhCl_3.3H_2O\text{-}Cu(ClO_4)_2]$

The catalytic oxidation of internal double bonds may be effected by the reaction of $RhCl_3.3H_2O\text{-}Cu(ClO_4)_2$ system in the presence of water, the Wacker-type cycle in the reaction proposed by Mimoun. (Scheme 4.1)[101]



Scheme 4.1: The mechanism for the Rh Catalysed Wacker-type oxidation of polybutadiene.

The above mechanism is similar to that of the Wacker type reaction in which the nucleophilic attack of the hydroxide anion on the olefin coordinated to the metal in its higher oxidation state give both the carbonyl compound and the reduced metal, which has to be reoxidised by a cooxidative reagent, e.g. copper, to make the reaction catalytic. [60]

Butan-2-one was obtained by Mimoun from *cis*-but-2-ene using this $RhCl_3.3H_2O\text{-}Cu(ClO_4)_2.6H_2O$ system, therefore, it was used in an attempt to oxidise *cis*-1,4-polybutadiene to yield the polyketone.

Mimoun has shown that internal double bonds are slower to oxidise than terminal double bonds and that the rate of oxidation of both can be increased by the presence of an ethanolic solution. Consequently, an ethanolic solution of *cis*-1,4-polybutadiene was treated with an $RhCl_3.3H_2O$-$Cu(ClO_4)_2.6H_2O$ in the presence of water, while oxygen was bled into the flask while refluxing over 24 hours.

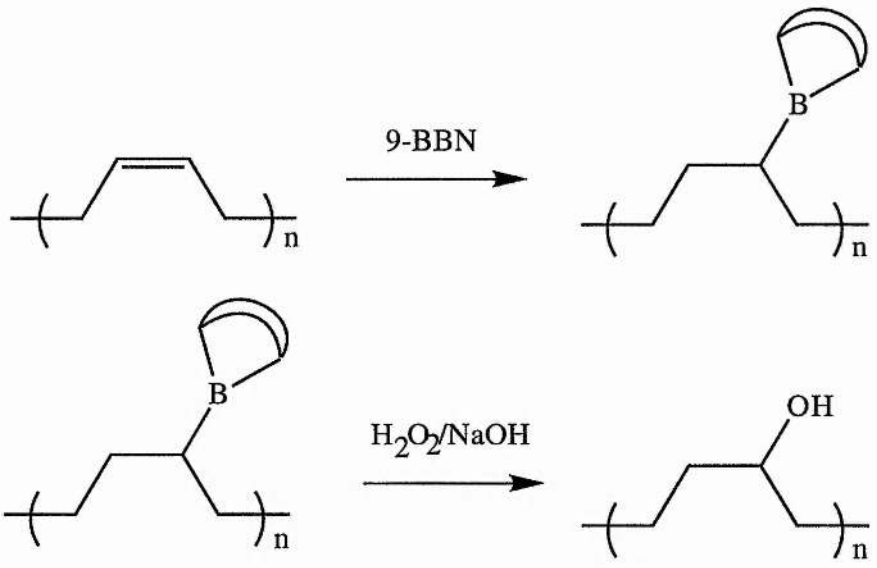
The products from the reaction were analysed by NMR and FTIR but unfortunately no characteristic carbonyl resonance were observed. Merely passing oxygen through the solution may not be effective enough, as reactions reported in the literature[68,101] require more forcing conditions, i.e. reactions under oxygen pressure to obtain higher concentrations.

4.2 HYDROBORATION-OXIDATION OF POLYBUTADIENE

Polybutadiene can be hydroborated to polyorganoboranes which easily undergo oxidation to the polyalcohol.

Initially our work has concentrated on a method by Chung and coworkers [110] in which polybutadiene is treated with 9-borabicyclononane (9-BBN) at -10°C to give the hydroborated polymer, followed by oxidation to the polyalcohol with $NaOH/H_2O_2$ at -25°C. (Scheme 4.2).

Hydroboration of polybutadiene followed by oxidation to the polyalcohol.



Scheme 4.2: Hydroboration-oxidation of polybutadiene using 9-BBN / NaOH and H_2O_2

The selectivity of the hydroborane (9-BBN) for the 1,2- and 1,4-position of the double bonds in polybutadienes is also discussed by Chung and coworkers.[110] Although the 1,2-microstructure is hydroborated selectively over the 1,4-microstructure, the 1,4-position is found to be easily hydroborated in the absence of the 1,2-microstructure.

The first reaction carried out using this method gave a 50% conversion to the polyalcohol, see ^1H NMR spectrum 4.1 on page 156. Characteristic resonances for the alcohol units are observed at 1.5 and 3.5 ppm, also observed are characteristic double bonds from *cis*-polybutadiene at 2.1 and 5.4 ppm.

Using a similar method by Ramakrishnan[69] in which the only difference was increased temperature and time, *cis*-1,4-polybutadiene was hydroborated at 50-70°C for 16-24 hours and then the oxidation was carried out at 0°C and allowed to warm to room temperature before being heated to 50-60°C for another 16-24 hours.

The polybutadiene alcohol from this reaction exhibited a 100% conversion to the polyalcohol as can be seen from the ^{1}H NMR and ^{13}C NMR spectra 4.2 and 4.3 on pages 157 and 158. In which the ^{1}H NMR shows the characteristic methine (CH) resonance from the hydroxyl substituted carbon atoms of the polybutadiene alcohol at 3.5 ppm and the methylene (CH_2) resonance at 1.5 ppm. The absence of characteristic vinyl protons at 5.4 ppm suggests complete conversion of the backbone double bonds, which is confirmed by the lack of a characteristic double bond resonance at 130 ppm for the *cis*-1,4-polybutadiene in the ^{13}C NMR.

The presence of two sites on the double bond for hydroboration-oxidation means that 3 diol segments are always generated, 1,4-, 1,5- and 1,6-diol segments (figure 4.1).

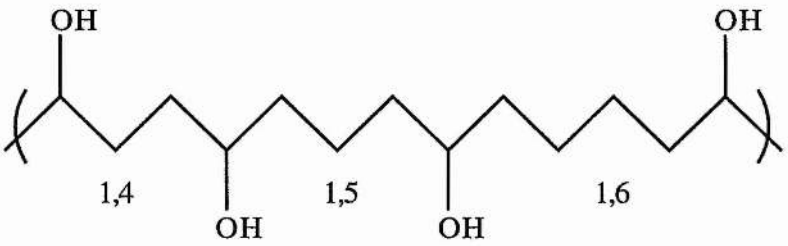


Figure 4.1: Polybutadiene alcohol with a 1,4-, 1,5- and 1,6-microstructure.

The ^{1}H NMR spectrum shows only one type of methine proton at 1.5 ppm, however, the presence of diol segments in the copolymers can be proved and quantified by ^{13}C NMR. Some fine structure is observed due to the chemical shift differences between the methine carbons corresponding to the 1,4-, 1,5- and 1,6-diols. The concentration of the three diol segments can be calculated from the relative intensities of the peaks that arise specifically due to one of these diol units. The mole percent of the 1,4-diol segment can be calculated by comparing the intensity of the peak at 34.9 ppm for the C_{β}'s of the 1,4-segment with the peaks at 27.0 and 23.0 ppm for the C_{γ}'s of the 1,6-diol and 1,5-diol respectively which shows the ratio of 1,4:1,5:1,6 was 1:1:1. Since the C_{γ} carbon peak of the 1,5-diol segment (23.0 ppm) represents only one carbon, while all the other peaks represent two carbon atoms in each segment, the intensity of the former peak is doubled therefore the ratio of 1,4:1,5:1,6 was 1:2:1.

An advantage of this route to the polyketone is that polyalcohols obtained will have some irregularity in the polymer chain. This irregularity is due to the two sites on the double bond for hydroboration which generates three types of diol segments 1,4 , 1,5 and 1,6 in a 1:2:1 ratio calculated from relative intensities using ^{13}C NMR DEPT spectrum, page 158. Hence, the irregularity in the polyalcohol chain will be carried through to the polyketone when prepared.

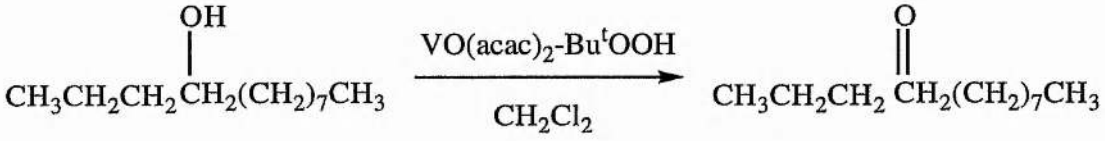
As this reaction has been shown to be successful in preparing a fully oxidised polybutadiene to give the corresponding alcohol it has been decide that further conversion of this polymer to a ketone via the oxidation of the secondary alcohol would be of interest.

4.2.1 OXIDATION OF SECONDARY ALCOHOLS IN POLYBUTADIENE ALCOHOL

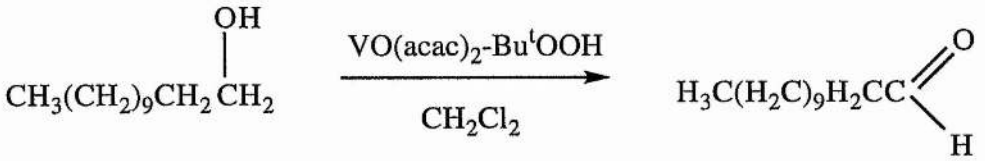
Various methods of converting a secondary alcohol to a ketone are presently available we have applied some of these methods to the oxidation of the polybutadiene alcohol which is prepared from the oxidation-hydroboration of polybutadiene with $NaOH/H_2O_2$ and 9-BBN. The methods studied include oxidation of the alcohol using $VO(acac)_2$ and Bu^tOOH,[102] activated DMSO with oxalyl chloride[103] and 4-methoxy-2,2,6,6-tetramethylpiperdinium chloride.[104,105]

4.2.2 OXIDATION OF SECONDARY ALCOHOLS IN POLYBUTADIENE ALCOHOL USING $VO(acac)_2$ AND Bu^tOOH

Oxidation of alcohols using a $VO(acac)_2$-Bu^tOOH system has been shown by Kaneda[102] and coworkers exclusively to oxidise secondary hydroxyl functions to ketones, since diols containing primary and secondary alcohols gave ketoalcohols as the only product. In addition, oxidation of 4-dodecanol and 1-dodecanol showed that the secondary alcohol were oxidised exclusively to the ketone, as the ratio of 4-dodecanone to 1-dodecanal was more than 10^2 (Equation 4.4 and 4.5).



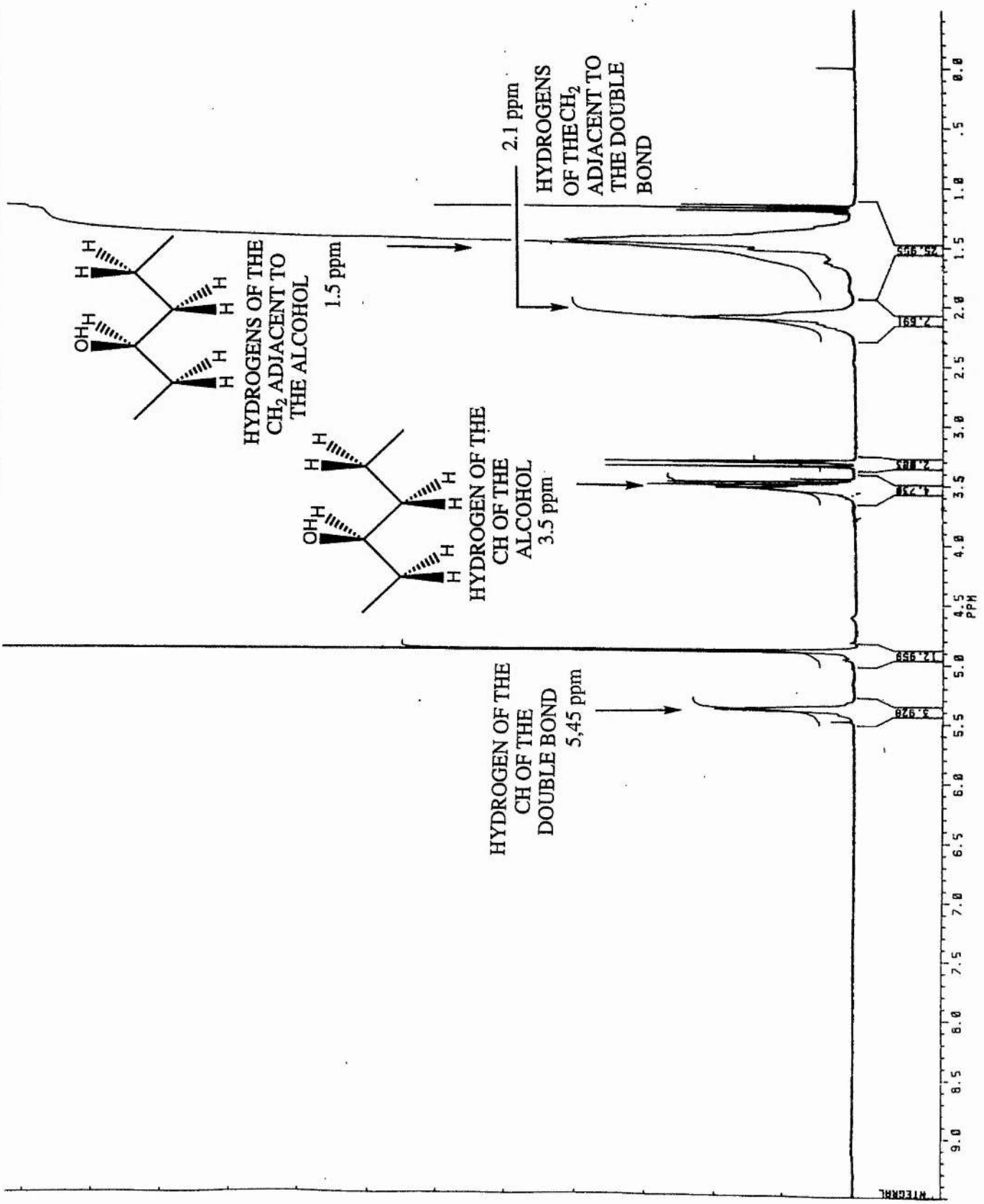
Equation 4.4: Oxidation of a secondary alcohol to ketone using $VO(acac)_2$.



Equation 4.5: Oxidation of a primary alcohol to aldehyde using $VO(acac)_2$.

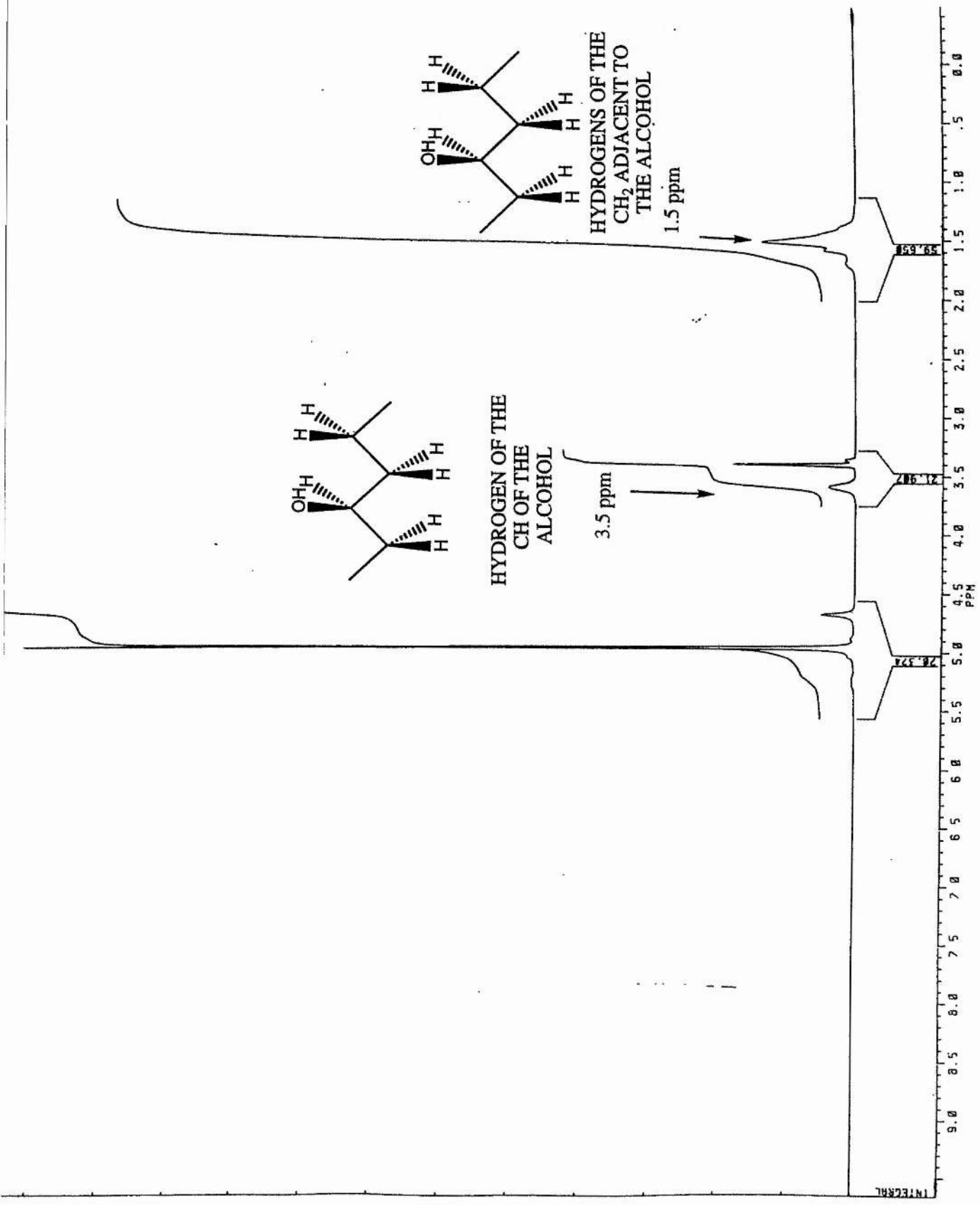
Spectrum 4. 1

Polyalcohol (LMWT-PBD) - ^{1}H NMR



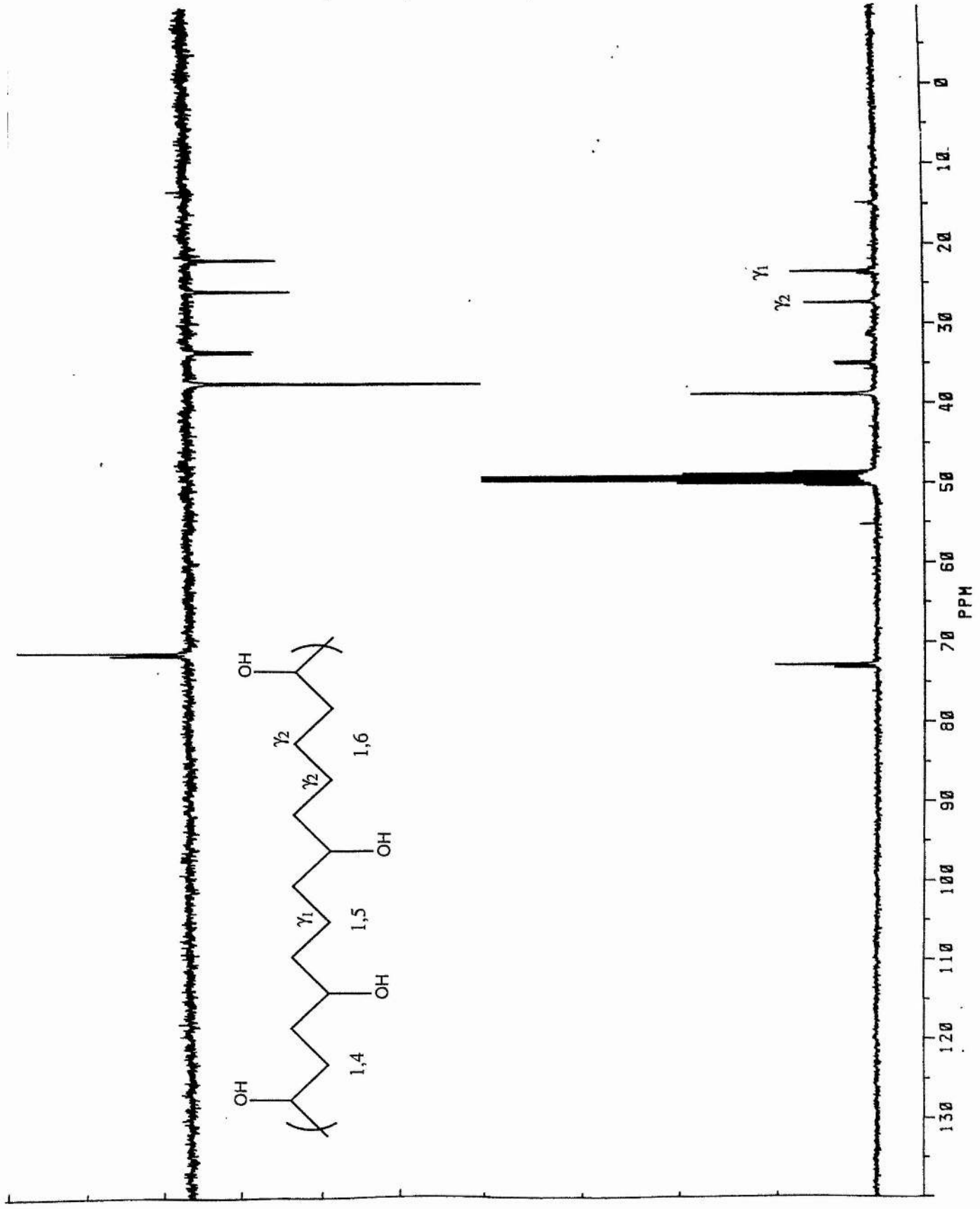
Spectrum 4. 2

Polyalcohol (LMWT-PBD) - ^{1}H NMR



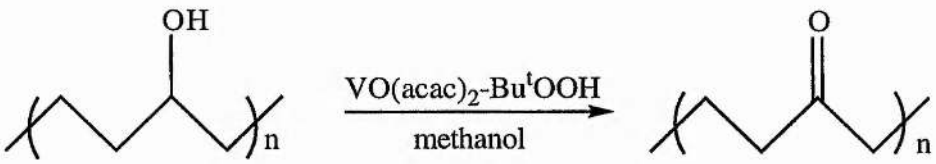
Spectrum 4.3 and 4.4

Polyalcohol (LMWT-PBD) - ^{13}C and DEPT NMR



In general the reaction involves the addition of the $VO(acac)_2$ catalyst to a solution of the alcohol and oxidant (Bu^tOOH) in benzene, this is allowed to react under reflux for 6-24 hours, depending on the alcohol being oxidised.

The selective oxidation of secondary alcohols over primary alcohols is an advantage when applying this system to the oxidation of polybutadiene alcohol as methanol is a good solvent for this polymer (Equation 4.6).



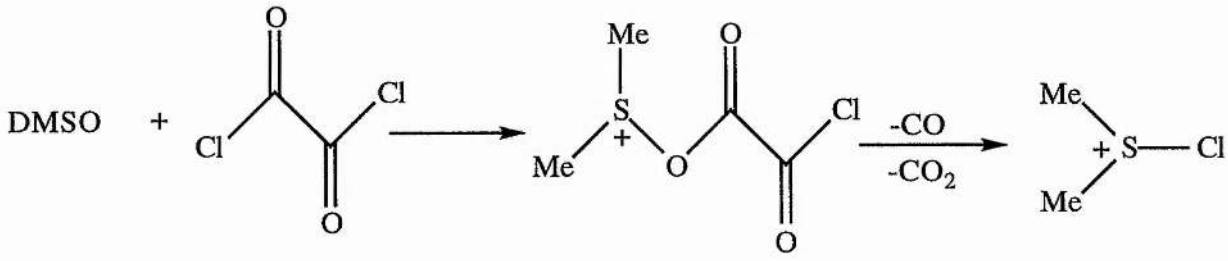
Equation 4.6: Oxidation of a secondary alcohol to ketone using $VO(acac)_2$ in Methanol

The Bu^tOOH oxidant was added to a methanol solution of the polybutadiene alcohol which was then added to the pre-weighed $VO(acac)_2$ catalyst. Addition of the polymer/Bu^tOOH solution to the dark green $VO(acac)_2$ resulted in the formation of a dark red/brown solution. The solution was then allowed to reflux, after only 15 minutes the polymer had precipitated out of solution. The solution and solid polymer were therefore separated, the solid polymer was easily re-dissolved in methanol and analysed by NMR which indicated that there was no change to the polybutadiene alcohol. NMR of the residual reaction solution showed no polymer to be present. If the methanol was attacked by the $VO(acac)_2$-Bu^tOOH system it would have produced formaldehyde which would have volatilised and therefore should not have affected the reaction. It is not certain why the polymer precipitated from the reaction, however several attempts to use this system for the oxidation of the polybutadiene alcohol resulted in its precipitation from the reaction solution. The polymer is not crosslinked as it dissolves readily in fresh methanol, this would indicate that the reaction solution is changed in some way making the polymer insoluble.

4.2.3 OXIDATION OF SECONDARY ALCOHOLS IN POLYBUTADIENE ALCOHOL WITH ACTIVATED DMSO USING OXALYL CHLORIDE

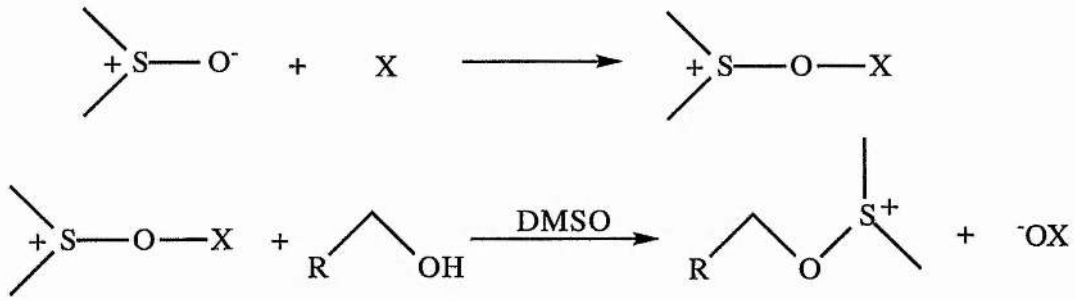
The most popular oxidation by dimethyl sulfoxide (DMSO) involves the use of oxalyl chloride to activate the dimethyl sulfoxide, which is commonly referred to as the Swern oxidation.[103] The advantages of this method are: the mild conditions; the ease of work-up, due to two of the main by products being carbon monoxide and carbon dioxide and that the reaction is usually very rapid.

Activation temperatures of about -60°C are typically used to form the activated dimethyl sulfoxide intermediate, which arises by spontaneous loss of carbon dioxide and carbon monoxide from an initially formed salt (Equation 4.7).



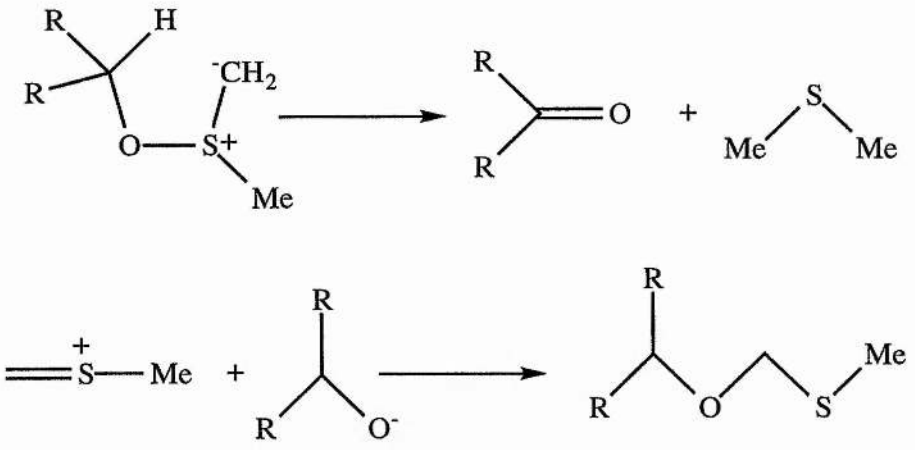
Equation 4.7: Formation of activated DMSO salt.

The initial product formed when an alcohol does attack the activated dimethyl sulfoxide is known to be the sulfonium salt (Scheme 4.3).



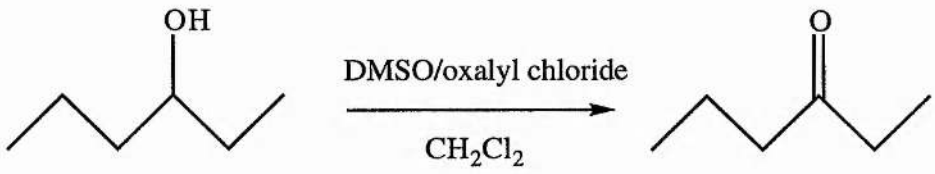
Scheme 4.3: Attack of the alcohol onto the activated DMSO to give a sulfonium salt.

The reaction then requires the addition of a base (commonly triethylamine) and results in the formation of an ylide (Scheme 4.4), which collapses intramolecularly to the carbonyl compound.



Scheme 4.4: Addition of the triethylamine to form the carbonyl compound.

Reactions of dimethyl sulfoxide (DMSO) with electronic "activators" such as oxalyl chloride, has proven highly useful in the oxidation of alcohols, diols and polyols to carbonyls.(Equation 4.8).



Equation 4.8: General reaction of DMSO/oxalyl chloride in CH_2Cl_2.

DMSO/oxalyl chloride reactions involved the formation of the activated DMSO species by adding a CH_2Cl_2 solution of DMSO to a CH_2Cl_2 solution of oxalyl chloride at -60°C, followed by the addition of a CH_2Cl_2 solution of the alcohol which was allowed to react for 15 minutes before triethylamine was added. The reaction solution was then allowed to warm to room temperature before water was added to the reaction solution to remove the carbonyl compound. This was then washed with dilute HCl, water and dilute Na_2CO_3.[103]

In an attempt to oxidised polybutadiene alcohol to the ketone the above method was studied. However, the polybutadiene alcohol is not soluble in CH_2Cl_2 but was found to dissolve in DMSO. Consequently the activated DMSO was prepared at -60°C without the presence of a solvent, to this was added a DMSO solution of the polybutadiene alcohol which was allowed to stir for 15 minutes before triethylamine was added. The reaction mixture was then allowed to warm to room temperature which resulted in a solid product which was insoluble in every common organic solvent and too sticky to carry out ^{13}C solid sate NMR analysis.

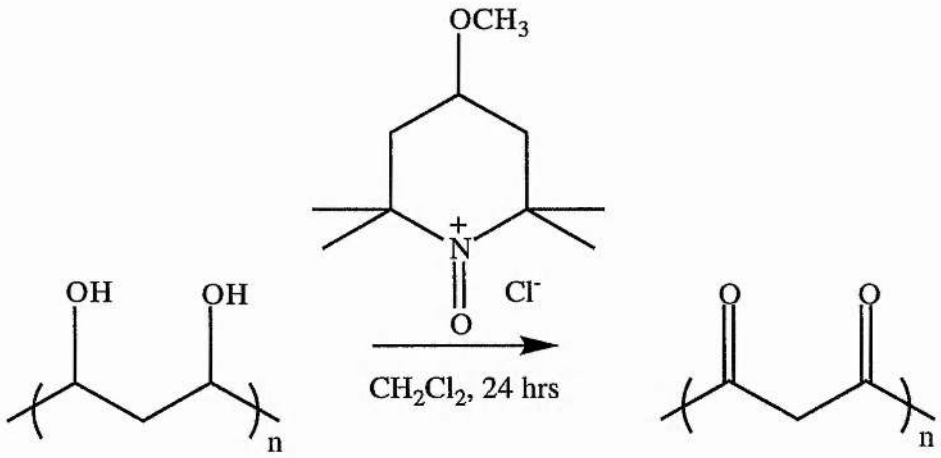
As the polyalcohol also dissolved in dimethylformamide (DMF) the subsequent reaction was carried out in DMF. The reaction was carried out as described above and when the

reaction solution was warmed to room temperature a solid product was observed which was found to be insoluble in common organic solvents. It was difficult to analyse this product as it was too rubbery to be packed into the rotor for ^{13}C solid state NMR and the IR was masked by the presence of DMF. The polymer was therefore washed with water to remove the DMF and then with diethyl ether to remove any trace of water and dried under vacuum. Analysis by IR of the washed polymer indicated the presence of the alcohol but not the carbonyl groups.

4.2.4 OXIDATION OF SECONDARY ALCOHOLS IN POLYBUTADIENE WITH 4-METHOXY-1-OXO-2,2,6,6-TETRAMETHYLPIPERIDINIUM CHLORIDE

4-methoxy-1-oxo-2,2,6,6-tetramethylpiperidinium chloride is known as an oxidising agent for the oxidation of alcohols to ketones.

Oxidation of polyvinylalcohol and hydroxyl terminated hydrogenated polybutadiene using 4-methoxy-1-oxo-2,2,6,6-tetramethylpiperidinium chloride has been reported by T. Endo and coworkers,[104] in which polymers containing carbonyl groups are obtained by dissolving 4-methoxy-1-oxo-2,2,6,6-tetramethylpiperidinium chloride in a suitable solvent (CH_2Cl_2), which does not dissolve the polymer or contain hydroxyl groups, where 100 parts of polyvinylalcohol is reacted with 1 part 4-methoxy-1-oxo-2,2,6,6-tetramethylpiperidinium chloride under nitrogen without light for 24 hours. (Equation 4.9).



Equation 4.9: Oxidation of polyvinyl alcohol using 4-methoxy-TEMPO-chloride in CH_2Cl_2.

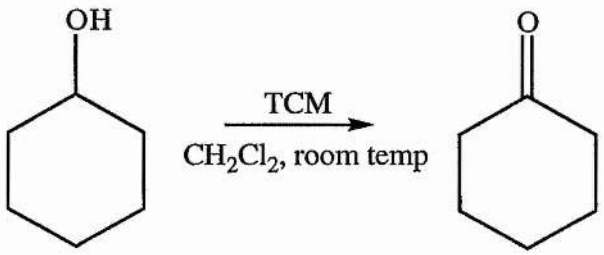
We have applied this system to the oxidation of polybutadiene alcohol, obtained by hydroboration-oxidation discussed earlier (see page 153), in an attempt to convert the secondary alcohols of the polybutadiene alcohol to the corresponding ketone.

A CH_2Cl_2 solution of the 4-methoxy-1-oxo-2,2,6,6-tetramethylpiperidinium chloride was added to the dispersed polybutadiene alcohol/CH_2Cl_2 solution in the absence of light and left to react for 24 hours. The product polymer was washed several times with CH_2Cl_2 and vacuumed dry. The polymer then re-dissolved in methanol without any problems indicating no reaction, this was later confirmed by NMR. It was therefore, thought that the reaction time may require lengthening, consequently the following reaction was carried out for 48 hours, but resulted in only the polybutadiene alcohol starting material.

Unfortunately, the product polymer when washed and analysed by NMR indicated no change. It is possible that the dispersion of the polymer in the solution is not fine enough to allow an interaction of the 4-methoxy-1-oxo-2,2,6,6-tetramethylpiperidinium chloride with the polybutadiene alcohol.

4.2.5 SELECTIVE OXIDATION OF ALCOHOLS WITH TRICHLOROMELAMINE

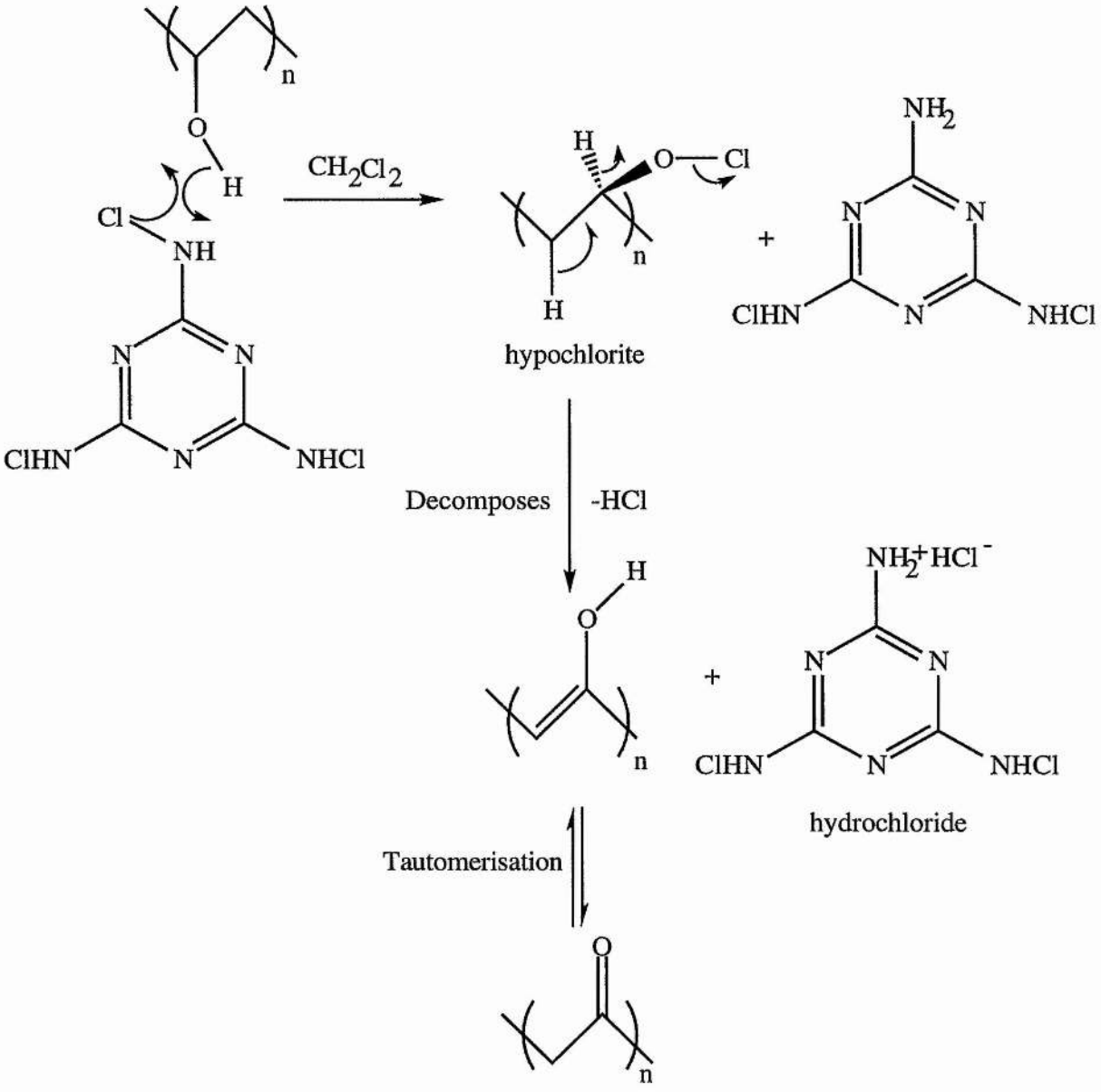
Kondo reported[107] a simple and selective oxidation of the alcohols to the corresponding carbonyl compounds using trichloromelamine (TCM). Cyclohexanol has been shown to react with TCM in CH_2Cl_2 at room temperature for three hours to give cyclohexanone in 90% yield (Equation 4.10).



Equation 4.10: Oxidation of cyclohexene to cyclohexanone using TCM in CH_2Cl_2.

Generally, secondary alcohol such as cyclohexanol, ∝-phenylethyl alcohol and 2-octanone are rapidly oxidised to their corresponding ketones in high yield. The oxidation of diols containing both primary and secondary hydroxyl groups were examined, in which it was demonstrated the secondary alcohols are preferentially oxidised. The proposed mechanism for this reaction is shown in scheme 4.5.

This reaction was initially carried out using polyvinylalcohol as the alcohol substrate and the polymer was dispersed in the CH_2Cl_2 solution as was the case in the 4-methoxy-1-oxo-2,2,6,6-tetramethylpiperidinium chloride reaction of polyvinylalcohol in CH_2Cl_2.



Scheme 4.5: The mechanism for the oxidation of polyvinylalcohol to a polyketone using TCM.

This route was abandoned because no change in the polyvinylalcohol was observed by IR or NMR, indicating the solubility of the polymer in dichloromethane was a problem. Therefore, the diol of polybutadiene discussed later (see page 171), prepared in a dichloromethane solution, was used to overcome the substrate solubility problem experienced by the polyvinylalcohol. Polybutadiene was partially converted to the diol using the epoxidation reaction without molecular sieves. The table below shows the percentage conversion to the diol and epoxide.

TABLE 4.1

		% CONVERSION		% UNREACTED
REACTION	MOLECULAR SIEVES	EPOXIDE *cis*	DIOL	DOUBLE BONDS
1a	-	88	12	NONE
2a	-	66	33	NONE

a - Starting material was polybutadiene with 99% *cis* double bonds (M.W.= 2-300,000)

Initially, the amount of diol was too low and therefore it was difficult to observe if any carbonyl groups were present after reaction with trichloromelamine. Although the second reaction showed a larger conversion to the diol still no carbonyl formation could be observed. During both reactions it was noted that the trichloromelamine seemed only partially soluble in the dichloromethane, or merely dispersed within the solution.

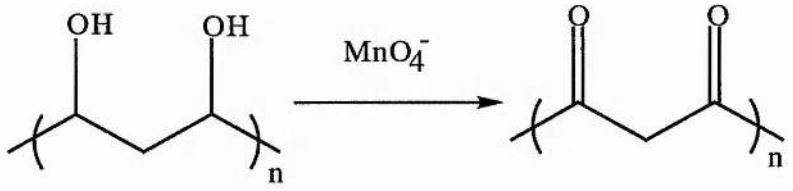
Detection of carbonyl groups have been hindered by low levels of diol present in the polymer, which, if only slightly converted to the ketone may not have been sufficient enough to detected by ^{13}C NMR.

CHAPTER FIVE

FUTURE WORK

5.1 A POLYKETONE FROM A POLVINYLALCOHOL

Hassan has suggested[108] that polyketones can be prepared by the oxidation of polyvinylalcohols with the permanganate ion as the oxidising agent. The reaction equation for this is shown below:



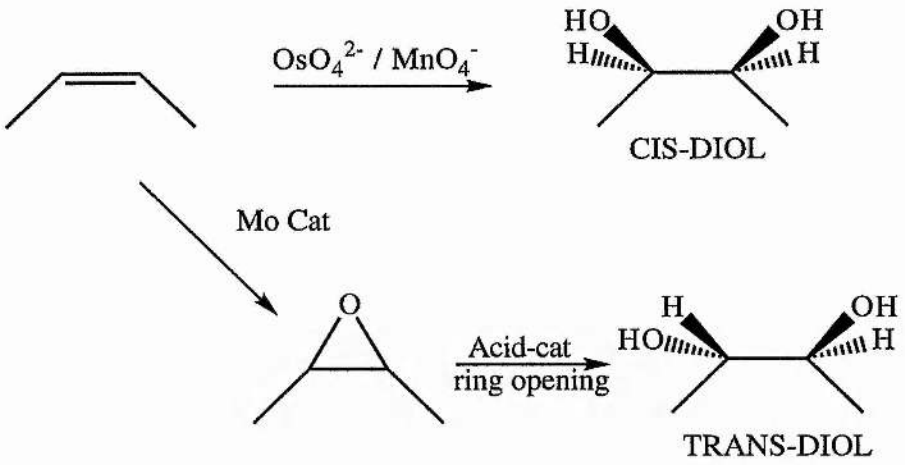
Equation 5.1: Oxidation of polyvinylalcohol to the ketone using the permanganate ion in CH_2Cl_2.

The oxidation involved treatment of a polyvinylalcohol solution with a potassium permanganate and sodium fluoride solution (pH 12.6) and is dependent on the pH of the medium and the stoichiometric concentration of the oxidant. The MnF_4 formed is removed from the filtrate which is then acidified (pH 5) to give the polyvinylketone. The reaction can be monitored via UV/VIS as the absorption maximum of the MnO_4^- ion at 526 nm decreases, with a simultaneous increase of the absorbances of the complex at 606, 435, and 350 nm. In addition, the disappearance of the absorption bands for the OH groups, indicates complete conversion to the ketone which is observed at 1650 cm^{-1}.

Such a system may be used for the oxidation of polyalcohol of polybutadiene, prepared using 9-BBN/NaOH (see chapter 4, page 153). Although a suitable solvent system for both polymer and reactants would require investigation, this would result in the desired polyketone (i.e. with additional carbon atoms between the carbonyl groups).

5.2 DIHYDROXYLATION OF POLYBUTADIENE

Dihydroxylation of a double bond can result in either a *trans* diol or a *cis* diol.[111] A *cis* diol is formed using either the osmium tetroxide or permanganate ion, as they are highly specific for *cis* hydroxylation. The *trans* diol on the others hand, generally results when the hydroxylation route proceeds via epoxide formation and its subsequent acid-catalysed ring opening (Scheme 5.1).



Scheme 5.1: Hydroxylation of alkene to *cis*- and *trans*-diols.

5.2.1 *cis*-HYDROXYLATION USING AD-MIX

Sharpless and coworkers[112] have developed an asymmetric dihydroxylation (AD) -mix (page 175) which contains a non-volatile source of osmium tetroxide and is ideal for *cis*-hydroxylation. A model reaction was carried out using the AD-mix in which *cis*-3-heptene was successful converted to heptane-3,4-diol (see ^{13}C NMR, spectrum 5.1, on page 169). Characteristic resonances for the diol formation are observed at 75 and 77 ppm although some remaining characteristic double bond resonances at 129 and 131 ppm are also observed, indicating that the method and technique being employed were effective although complete conversion was not achieved.

A series of reactions on polybutadiene as shown in table 5.1 were then investigated in an attempt to find a suitable solvent system for the polymer and other reactants (i.e. AD-mix).

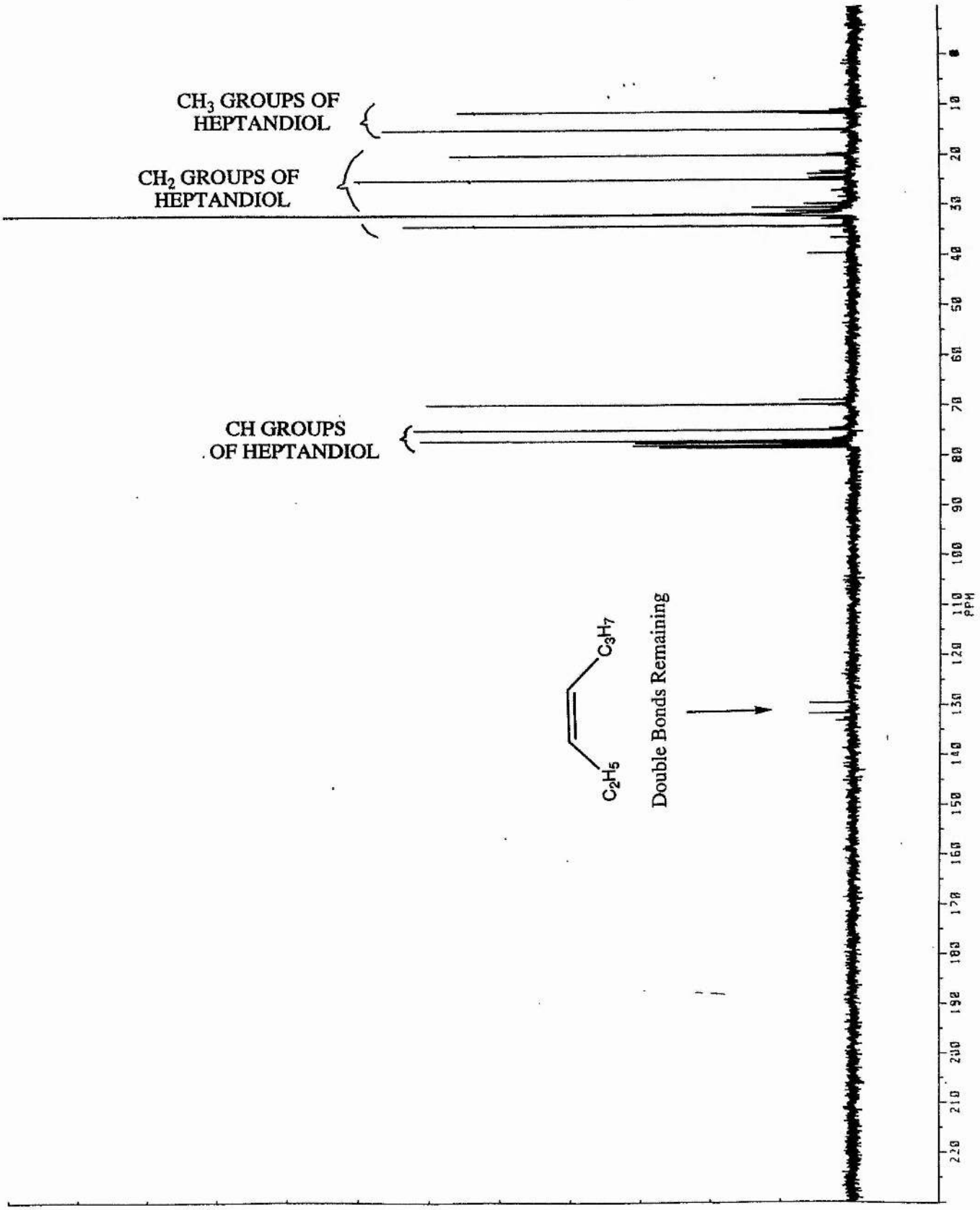
TABLE 5.1

DIHYDROXYLATION OF POLYBUTADIENE USING THE AD-MIX

Reaction Number	Substrate	Catalyst	Solvent system	Phase Transfer Agent
1	PBD	OsO_4	CH_2Cl_2	-
2	PBD	OsO_4	THF	-
3	PBD	OsO_4	THF/H_2O	-
4	PBD	OsO_4	CH_2Cl_2/H_2O	
5	PBD	OsO_4	CH_2Cl_2/H_2O	√

Spectrum 5.1

Heptandiol (*cis*-3-heptene) - ^{13}C NMR



Products analysed from these reactions showed no presence of alcohols. Although visual observation indicated that the best solvent system for the polymer and AD-mix was CH_2Cl_2/H_2O (as the dichloromethane dissolves the polymer and the water dissolves the AD-mix) it is not known whether the osmium tetroxide is generated in this solvent system. The asymmetric dihydroxylation reactions by Sharpless and coworkers[112] were carried out in a t-BuOH/H_2O system in which partial miscibility occurs between the two solvents allowing transfer of the reactants. Therefore, it was thought that further investigations with the CH_2Cl_2/H_2O solvent system involving the incorporation of a phase transfer agent may be successful in the preparation of a polyalcohol, reaction 5 in table 5.1 above. In reaction 5 no polymer was detected in the organic layer indicating that the polyalcohol product may be water soluble. If this is the case then further studies should focus on extraction of the polymer from the aqueous layer using acetic acid, which will acetylate the polymer making it insoluble in the aqueous layer. Alternatively, the water can be evaporated from the aqueous layer then reacted with acetic anhydride.

5.2.2 *cis*-HYDROXYLATION USING PERMANGANATE ION

The hydroxylation using potassium permanganate is well known and has proved to be a useful method for this type of conversion. This route was therefore investigated as a means of preparing a polyalcohol with a *cis*-diol microstructure.

From the literature, the optimum solvent system for this type of reaction was shown to be t-BuOH/H_2O,[112] similar to that of the osmium tetroxide dihydroxylation. As discussed previously polybutadiene will not dissolve in t-BuOH, therefore, a series of reactions was carried out using various solvent systems as shown in the table below.

TABLE 5.2

DIHYDROXYLATION OF POLYBUTADIENE USING PERMANGANATE

Reaction Number	Substrate	Catalyst	Solvent system	Phase Transfer Agent
1	PBD	MnO_4	CH_2Cl_2	-
2	PBD	MnO_4	THF	-
3	PBD	MnO_4	THF/H_2O	-
4	PBD	MnO_4	CH_2Cl_2/H_2O	-
5	PBD	MnO_4	CH_2Cl_2/H_2O	√

Unfortunately, in reactions 1-4 no alcohol was observed; however, in reaction 5 no polymer was detected in the organic layer indicating that the polyalcohol product may be water soluble. This is the same as with the previous set of experiments, which support the previous rational, that the polymer is water soluble and could therefore be removed by acetylation.

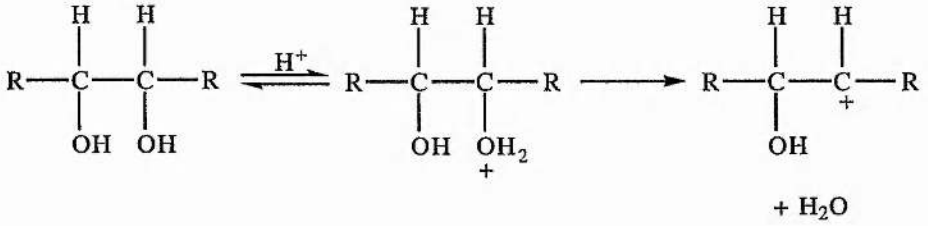
5.2.3 *trans*-HYDROXYLATION USING WATER / MoO_2CL_2 (DIETHOXYPHOSPHORYL CAMPHOR)

Previous work in this area indicated that adventitious water in the epoxidation reaction caused ring opening of the epoxide to form a diol.[72] Some reactions were therefore carried out in which water was added to the already formed epoxide and refluxed overnight. Some diol formation was observed but the epoxide resonance had not been significantly reduced.

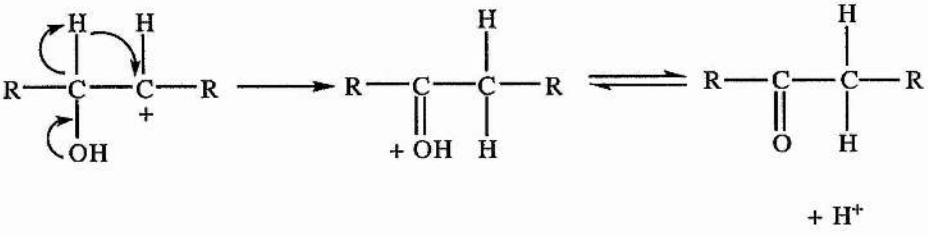
Diol formation in the previous epoxidation reactions may not have been the result of water alone but the presence of the catalyst may have had an influence. It is known that the presence of water in the epoxidation reaction also produces a less active epoxidation catalyst,[73] indicating some interaction between the catalyst and water. It has been recently shown that the reaction is very sensitive to the amount of water used. One drop is effective however two drops can destroy the catalyst[113]. The water used in the aforementioned reactions may have been too much for the catalyst and therefore the epoxide was not fully converted to the diol. Subsequent investigations, therefore, would involve a controlled addition of water and a further addition of the molybdenum catalyst.

5.3 DEHYDRATION OF THE POLYALCOHOL TO POLYKETONE

The polydiol prepared by the above suggested methods can then be converted to the polyketone via a pinacol rearrangement. The pinacol rearrangement[114] is believed to involve two important steps: (1) loss of water from the protonated diol to form a carbocation (equation 5.2); (2) rearrangement of the carbocation by a 1,2-shift to yield the protonated ketone. (equation 5.3).



Equation 5.2: Formation of a carbocation from an alcohol under the influence of acid.

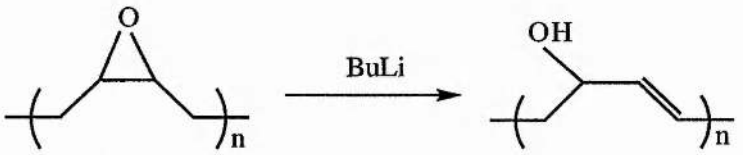


Equation 5.3: Rearrangement of the carbocation by a 1,2-shift to yield the protonated ketone.

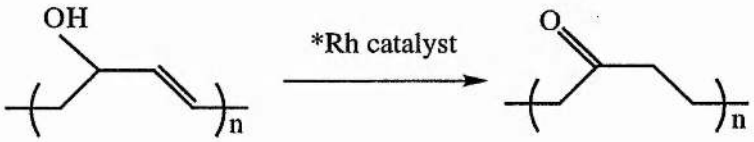
5.4 ALTERNATIVE ROUTE TO POLYKETONES

5.4.1 PREPARATION OF A POLYKETONE VIA AN ALLYLIC ALCOHOL

Further investigation into obtaining a polyketone may follow a route via an allylic alcohol. The proposed reaction involves isomerisation of the polyepoxide using n-butyl lithium to give the allylic alcohol[72] (equation 5.4), followed by reaction with $[Rh\{P(OC_6H_4)(OPh)_2\}\{P(OPh)_3\}_3]$ complex which is a highly effective catalyst for the isomerisation of allylic alcohols to ketones[115], as shown in equation 5.5.



Equation 5.4: Formation of an allylic alcohol from the reaction of the epoxide with butyl lithium.



Equation 5.5: Formation of the ketone from the reaction of the allylic alcohol with Rh catalyst.

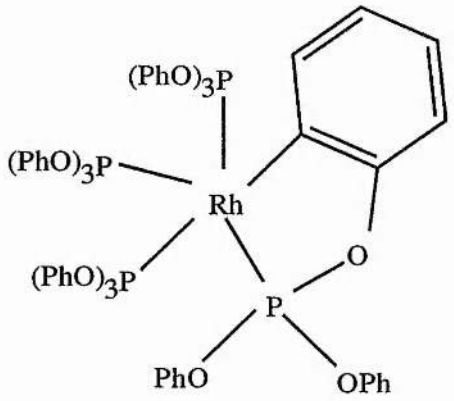


Figure 5.1: $[Rh\{P(OC_6H_4)(OPh)_2\}\{P(OPh)_3\}_3]$ catalyst.

Problems with crosslinking may be avoided using this route as all the epoxide rings would be opened by the reaction with n-butyl lithium. Therefore, when reacted with the $[Rh\{P(OC_6H_4)(OPh)_2\}\{P(OPh)_3\}_3]$ catalyst to form the polyketone no crosslinking should occur.

CHAPTER SIX

EXPERIMENTAL

6.0 EXPERIMENTAL

6.1 ANALYTICAL TECHNIQUES

1. NMR Spectroscopy

NMR spectra were recorded on a Brüker Associates AM300 spectrometer (300MHz) operating in the Fourier-transform mode with noise proton decoupling for ^{13}C. All polyepoxides and polyketones were analysed in $CDCl_3$ and all polyalcohols were analysed in methanol-d_4.

2. Infra-red Spectroscopy

IR spectra were recorded on a Perkin-Elmer 1710 Fourier Transform Infrared Spectrometer.

3. High Performance Liquid Chromatography (HPLC)

Chloride analysis was carried out using a Perkin-Elmer TriDet HPLC using a 0.02 M phthalic acid mobile phase with a spectra physics integrator and a UV detector.

4. Atomic Absorption (AA)

Epoxidised polybutadiene and polyisoprene were analysed for molybdenum from the catalyst using a Philips PU9400X AAS.

5. Carbon, Hydrogen and Nitrogen Analysis

The Carbon, Hydrogen and Nitrogen analysis of the epoxidised polybutadiene and polyisoprene was performed on a Carlo ERBA 1106 analyser.

6. Thermal Gravimetric Analysis and Differential Thermal Analysis

The physical and chemical properties of epoxidised polybutadiene and polyisoprene were analysed using a SDT 2960 Simultaneous DTA-TGA. Each sample was analysed in ceramic pans in a nitrogen atmosphere using alumina as the reference sample.

6.2 SOLVENTS

Tetrahydrofuran and light petrol (40-60°C boiling range), diethyl ether and toluene were dried by distillation over sodium diphenylketyl. Dichloromethane, dimethylformamide and dimethylsulphoxide were dried by distillation over calcium hydride. Methanol and ethanol were dried over magnesium turnings, hexane was dried over sodium and dimethoxyethane and t-butanol were used as obtained from Lancaster and Aldrich respectively. Benzene was obtained from May and Baker Ltd in a pure crystallisable, sulphur free form.

6.3 STARTING MATERIALS

Calcium carbonate and potassium permanganate were from BDH, ρ-toluene sulphonic acid and rhodium trichloride trihydrate were purchased from Avacado. Ethane diol, sodium hydroxide, potassium hydroxide and magnesium sulphate were purchased from Fisons and tert-butylhydroperoxide (3.0 mol dm^{-3} anhydrous solution in 2,2,4-trimethylpentane) was purchased from Fluka. All other commercial starting materials were bought from Aldrich and used without further purification. The AD-mix[112] from Aldrich contains:

$K_2OsO_2(OH)_4$ - non-volatile source of OsO_4.
$(DHQ)_2PHAL$ - $(Dihydroquinine)_2$ Phthalazine.
->Ligand - Cinchona Alkaloid.
$K_3Fe(CN)_6$ - stoichiometric reoxidant, good system for Os catalysed dihydroxylation of alkenes.
K_2CO_3 - for BASIC conditions.

$[MoO_2Cl_2[(1R)\text{-endo}]\text{-}(+)\text{-}3$ (diethoxyphosphoryl)camphor], $[MoO_2Cl_2L]$, was made by a literature procedure.[73] Tri-n-butylphosphine oxide was prepared by Dr A Aitken.

6.4 AIR-SENSITIVE TECHNIQUES

All manipulations were carried out under oxygen-free nitrogen using standard Schlenk line and catheter tubing techniques.

6.5. EPOXIDATION

6.5.1 EPOXIDATIONS REACTIONS WITH POLYBUTADIENE IN DICHLOROMETHANE, CATALYST ADDED AT 0°C,[72] ROOM TEMPERATURE AND POLYISOPRENE WITH CATALYST ADDED AT ROOM TEMPERATURE.

Molecular sieves 4A[84] (10 g) were placed in a 100 cm^3 Schlenk flask under nitrogen and heated in a vacuum for 5 minutes. A solution of polybutadiene or polyisoprene both containing >99% *cis*-1,4 double bonds (0.54g / 0.68g respectively; 10 mmol of double bonds) in dichloromethane (40 cm^3) (also under nitrogen) was transferred from a second Schlenk flask via catheter tubing into the activated molecular sieves, where it was agitated by a magnetic stirrer. Tert-butylhydroperoxide (1.25 g; 13.89 mmol) in 2,2,4-trimethyl pentane (10 cm^3) was then added. The reaction mixture was left to stir for 30 minutes at room temperature.

Addition of $[MoO_2Cl_2L]$ catalyst (0.1 g; 0.21 mmol)(catalyst:alkene 50:1) dissolved in either tetrahydrofuran (10 cm^3) or dichloromethane (10 cm^3) was carried out at either 0°C over 10 minutes or room temperature, followed by stirring for eighteen hours at room temperature.

6.5.2 EPOXIDATION OF POLYDIENES WITHOUT THE ADDITION OF MOLECULAR SIEVES

Reactions without molecular sieves involving either polybutadiene or polyisoprene were carried out as described previously, leaving out the addition of the polyepoxide solution to the molecular sieves. Instead the oxidant and then the MoO_2Cl_2L catalyst were added to the polymer solution.

6.5.3 EPOXIDATION OF POLYBUTADIENE OR POLYISOPRENE USING A PREFORMED MoO_2-MOLECULAR SIEVES CATALYST COMPLEX

Molecular sieves 4A (10 g) were placed in a 100 cm^3 schlenk flask under nitrogen and heat in a vacuum for 5 minutes. $[MoO_2Cl_2L]$ catalyst (0.1 g; 0.21 mmol) in CH_2Cl_2 or THF (10 cm^3) was then added via catheter tubing to the activated molecular sieves and stirred for 15 minutes. The molecular sieves-MoO_2 complex was allowed to settle to the bottom of the flask before the solution containing free ligand and excess catalyst was removed by catheter.

A solution of polybutadiene or polyisoprene both containing >99% *cis*-1,4 double bonds (0.54 g / 0.68g respectively; 10 mmol of double bonds) in CH_2Cl_2 or THF (40 cm^3) (also under nitrogen) was transferred from a second schlenk flask via catheter tubing into the molecular sieves-MoO_2 complex, where it was agitated by a magnetic stirrer for 15 minutes

before tert-butylhydroperoxide (1.25 g; 13.89 mmol) in 2,2,4-trimethyl pentane (10 cm^3) was added. The reaction mixture was left to stir for 24 hours at room temperature.

6.5.4 PURIFICATION OF THE POLYBUTADIENE AND POLYISOPRENE

The epoxidised polybutadiene and polyisoprene solutions after being removed from the bulk of the molecular sieves were centrifuged to remove trace amounts of molecular sieves. Calcium carbonate (0.45 g; 0.42 mmol) was then added and the solution stirred for 30 minutes to remove any hydrochloric acid produced from the catalyst. The calcium chloride formed and any remaining calcium carbonate were then removed by centrifuged.

Finally the polymer was precipitated by adding the solution to petrol (100 cm^3) to remove any other impurities in the solution. The polymer was either re-dissolved in THF or CH_2Cl_2 (50 cm^3) and some was dissolved in $CDCl_3$ for NMR analysis, where as IR analysis allows the solvent (THF or CH_2Cl_2) to evaporate off leaving a polymer film on the plate.

6.5.5 THERMAL GRAVIMETRIC ANALYSIS AND DIFFERENTIAL THERMAL ANALYSIS OF THE EPOXIDISED POLYBUTADIENE AND POLYISOPRENE

The epoxidised polybutadiene and polyisoprene were analysed in ceramic pans, one pan contained the polymer being analysed and the other contained the reference alumina. The difference in weight and changes in thermal energy were recorded in a temperature range of 25-400°C heating at a rate of 10°C/min in a nitrogen atmosphere.

6.5.6 ELEMENTAL ANALYSIS

6.5.6.1 MOLYBDENUM ANALYSIS OF THE EPOXIDSED POLYBUTADIENE AND POLYISOPRENE BY ATOMIC ABSORPTION

The unpurified epoxidised polybutadiene and polyisoprene polymers (0.067g-0.126g) prepared with MoO_2Cl_2L catalyst and MoO_2-mol. sieves complex were dissolved in the minimum amount of hot concentrated nitric acid (3-6 cm^3) and then made up to the mark in a volumetric flask (100 cm^3) with distilled water for molybdenum analysis by atomic absorption. Each sample was analysed and compared to standard solution made from 1020 μgcm^{-3} molybdenum in H_2O with the previously used amount of nitric acid added to each standard as there is a small amount of molybdenum present in the acid.

Polyepoxides prepared using MoO_2Cl_2L complex

POLYMER	CATALYST	Theoretical Yield of Mo (ppm)	Actual Yield of Mo (ppm)	% Mo remaining in polymer	Weight of Catalyst used	Weight of polymer used
PBD	MoO_2Cl_2L	44	6.5	14.7	0.1234	0.54
PBD	MoO_2-mol sieves	47	5.7	12.1	0.2434	0.54
PISOP	MoO_2Cl_2L	40	29	72.5	0.1347	0.68
PISOP	MoO_2-mol sieves	40	8	20	0.2518	0.68

6.5.6.2 CHN ANALYSIS

The theoretical compositions of the epoxidised polybutadiene, $H\text{-}(CH_2CH{=}CHCH_2)_{3703\text{-}5555}\text{-}H$, is 68.6% carbon; 8.5% hydrogen and polyisoprene, $H\text{-}(CH_2C(CH_3){=}CHCH_2)_{3676}\text{-}H$ is 71.4% carbon and 9.5% hydrogen.

A comparison of the CHN analyses for the unpurified and purified polyepoxides shown below indicate that the composition of the purified polymers is very close to the theoretical composition above.

Unpurified:	polybutadiene epoxide:	(C : 56.53%, H : 7.34%)
	polyisoprene epoxide:	(C : 61.95%, H : 8.67%)
Purified:	polybutadiene epoxide:	(C : 65.90%, H : 8.23%)
	polyisoprene epoxide:	(C : 68.76%, H : 8.75%)

6.6. MOLYBDENUM CATALYST STUDY

6.6.1 LOW TEMPERATURE NMR

The behaviour of MoO_2Cl_2L catalyst was investigated using low temperature NMR studies. The MoO_2Cl_2L catalyst only (1), MoO_2Cl_2L and Bu^tOOH (2) and MoO_2Cl_2L, ButOOH and cyclohexene (3) were studied via ^1H and ^{31}P nmr in a temperature range of -50°C and 25°C. The spectroscopic results indicated that the organic ligand remained intact on the catalyst in each case, although after long reaction times (72 hours) and in the presence of Bu^tOOH free ligand was observed.

6.6.2 CHLORINE ANALYSIS

The reaction of the epoxidation catalyst MoO_2Cl_2L with molecular sieves, Bu^tOOH and cyclohexene was analysed for the formation of chloride (produced by the catalyst) by using HPLC.

Reaction of molecular sieves (10 g) with MoO_2Cl_2L catalyst (0.1 g) in CH_2Cl_2 (40 cm^3) and reaction of molecular sieves (10 g) and ButOOH (8 cm^3)(3M in isooctane) with MoO_2Cl_2L catalyst (0.1 g) in 40 cm^3 CH_2Cl_2 were compared to a standard solution (100 ppm of chloride) from an aqueous solution of sodium chloride. The results shown below indicate that the Bu^tOOH oxidant promotes the loss of the chloride.

		PPM
REACTION 1	MoO_2Cl_2L + mol. sieves	6.7
REACTION 2	MoO_2Cl_2L + mol. sieves + Bu^tOOH	127.5
STANDARD	Aqueous solution of NaCl.	100

6.7 ISOMERISATION

6.7.1 ISOMERISATION REACTION WITH n-Bu_3PO AS THE SOLUBILISER[96]

All of these reactions were carried out in a nitrogen atmosphere. A homogeneous solution of lithium bromide (0.4 g; 4.5 mmol) and tri-n-butylphosphine oxide (1.0 g; 4.5 mmol) in toluene (15 cm^3) was cathetered dropwise into a stirred solution of the polybutadiene epoxide (0.65 g; 9.3 mmol) dissolved in toluene (30 cm^3). A reflux condenser and nitrogen bubbler were attached to the reaction flask, and the mixture refluxed for one hour. The above procedure was also repeated for two and twenty-four hour periods. After the allotted time the reaction mixture was evaporated to dryness give a soluble polymer, which was re-dissolved in CH_2Cl_2 and analysed by NMR in which no carbonyl resonances were observed.

6.7.2 ISOMERISATION REACTION WITH HMPA AS THE SOLUBILISER

Method one: HMPA and polyepoxide reflux followed by the addition of LiBr.

All of these reactions were carried out in a nitrogen atmosphere. In general, a solution of the polybutadiene epoxide (0.7 g; 10 mmol) or polyisoprene epoxide (0.84g; 10 mmol) in benzene, CH_2Cl_2 or THF (50 cm^3) was used. HMPA (0.45 g; 2.5 mmol) was added to the stirred polyepoxide / epoxide solution, which was then refluxed for 15 minutes. The resultant mixture was allowed to cool, then cathetered into a flask containing LiBr (0.2g; 2.5 mmol) and allowed to stir for a few minutes The solution was then cathetered directly into a nmr tube for analysis and any solid products were removed for IR analysis.

Method two: Homogeneous solution of LiBr/HMPA added to polyepoxide.

All of these reactions were carried out in a nitrogen atmosphere. In general, a solution of the polybutadiene epoxide (0.7 g; 10 mmol) or polyisoprene epoxide (0.84g; 10 mmol) in benzene, CH_2Cl_2 or THF (50 cm^3) was prepared in the reaction flask. A homogeneous solution of LiBr (0.4 g; 5 mmol) and HMPA (0.9 g; 5 mmol) in benzene (30 cm^3), dichloromethane (30 cm^3) or tetrahydrofuran (30 cm^3) was cathetered into the solution. The reaction mixture was then refluxed for 15 minutes, after which the resultant mixture was washed with water to remove LiBr and HMPA. The washed benzene layer was then cathetered across to another schlenk where it was evaporated to dryness (leaving only a small solid polymer residue), distilled water was then added to the reaction flask, which precipitated the polymer, and both solids would not re-dissolve and were therefore analysed by IR.

Method three: Polyepoxide, LiBr and HMPA added together then refluxed.

All of these reactions were carried out in a nitrogen atmosphere. Typically, a solution of the polybutadiene epoxide (0.7 g; 10 mmol) or polyisoprene epoxide (0.84g; 10 mmol), lithium bromide (0.5 g; 5.7 mmol) and HMPA (1.0 g; 5.6 mmol) in benzene, CH_2Cl_2 or THF (50 cm^3) was prepared in the reaction flask. The reaction mixture was then refluxed for 15 minutes, after which the resultant mixture was washed several times with water to remove HMPA and LiBr. The washed organic layer was then cathetered across to another schlenk where it was evaporated to dryness (leaving only a small polymer residue). Distilled water was then added to the reaction flask which precipitated a solid polymer which would not re-dissolve and was therefore analysed by IR. One polybutadiene was analysed by solid state NMR in which a distinctive carbonyl resonance was observed.

NOTE

1. Reactions with varying amounts of lithium bromide to polyepoxide were carried out according to method two as this was shown by model reactions to be the most effective route to the ketone.

2. Model reactions were carried out with (0.5g) 2,3-epoxybutane according to method 1 and 2. Method 3 was the initial route studied for the isomerisation of polybutadiene epoxide.

6.7.3 ISOMERISATION REACTION WITH DMI AS THE SOLUBILISER

Method one: DMI and polyepoxide refluxed together followed by the addition of LiBr.

All of these reactions were carried out in a nitrogen atmosphere. In general, a solution of the polybutadiene epoxide (0.7 g; 10 mmol) or polyisoprene epoxide (0.84g; 10 mmol) in benzene, CH_2Cl_2 or THF (60 cm^3) was used. DMI (0.45g; 2.5 mmol) was added to the stirred polyepoxide/epoxide solution, which was then refluxed for 15 minutes. The resultant mixture was allowed to cool, then cathetered into a flask with LiBr (0.2g; 2.5 mmol) and allowed to stir for a 5 minutes. A sample of the (THF/CH_2Cl_2) solution was then cathetered directly into a NMR tube where nitrogen was bubbled through the solution to evaporate the majority of the solvent. $CDCl_3$ was then added to the remaining viscous solution and analysed, and any solid products from the reaction were analysed by IR.

Method two: Homogeneous solution of LiBr/DMI added to polyepoxide.

All of these reactions were carried out in a nitrogen atmosphere. In general, a solution of the polybutadiene epoxide (0.7 g; 10 mmol) or polyisoprene epoxide (0.84g; 10 mmol) in benzene, CH_2Cl_2 or THF (50 cm^3) was prepared in the reaction flask. A homogeneous solution of LiBr (0.4 g; 5 mmol) and DMI (0.9 g; 5 mmol) in benzene, CH_2Cl_2 or THF (30 cm^3) was cathetered into the solution. The reaction mixture was then refluxed for 15 minutes. A sample of the (THF/CH_2Cl_2) solution was then cathetered directly into a NMR tube where nitrogen was bubbled through the solution to evaporate the majority of the solvent. $CDCl_3$ was then added to the remaining viscous solution and analysed.

NOTE

Model reactions were carried according to method 1 and 2 using (0.5g) 2,3-epoxybutane.

6.7.4 ISOMERISATION REACTION WITH NO SOLUBILISER

All of these reactions were carried out in a nitrogen atmosphere. In general, a solution of the polybutadiene epoxide (0.7 g; 10 mmol) or polyisoprene epoxide (0.84g; 10 mmol) in CH_2Cl_2 or THF (50 cm^3) was used directly after the epoxidation reaction. LiBr (0.2 g; 2.5 mmol) was then dispersed in the stirred polyepoxide solution, which was then refluxed for 15 minutes. A sample of the (THF/CH_2Cl_2) solution was then cathetered directly into a NMR tube where nitrogen was bubbled through the solution to evaporate the majority of the solvent. $CDCl_3$ was then added to the remaining viscous solution and analysed. IR analysis was also carried out by adding a few drops of the solution to the NaCl plates and allowing it to evaporate leaving the polymer, the solid polymer was also analysed by IR analysis.

6.7.5 DERIVATISATION OF POLYKETONE WITH ETHYLENE GLYCOL

Method one

All of these reactions were carried out in a nitrogen atmosphere. In general, a solution of the low molecular weight polybutadiene epoxide (0.7 g; 10 mmol) in CH_2Cl_2 (50 cm^3) was used. HMPA (0.45 g; 2.5 mmol) and ethylene glycol (30 cm^3) were added to the stirred polyepoxide/epoxide solution, which was then refluxed for 15 minutes. The resultant mixture was allowed to cool, then cathetered into a flask with LiBr (0.2 g; 2.5 mmol) and allowed to stir for a few minutes.. A sample of the CH_2Cl_2 solution was then cathetered directly into a NMR tube where nitrogen was bubbled through the solution to evaporate the majority of the solvent. $CDCl_3$ was then added to the remaining viscous solution and analysed. Solid products were removed for IR analysis.

Method two

All of these reactions were carried out in a nitrogen atmosphere. In general, a solution of the low molecular weight polybutadiene epoxide (0.7 g; 10 mmol) in CH_2Cl_2 (50 cm^3) was used. Ethylene glycol (30 cm^3) and *p*-toluene sulphonic acid (0.05 g) were added to the stirred polyketone solution, which was then refluxed for 1 hour. The resultant mixture was allowed to cool, then cathetered into a flask with LiBr (0.2 g; 2.5 mmol) and allowed to stir for a few minutes. A sample of the (THF/CH_2Cl_2) solution was then cathetered directly into a NMR tube where nitrogen was bubbled through the solution to evaporate the majority of the solvent. $CDCl_3$ was then added to the remaining viscous solution and analysed. Solid products were removed for IR analysis.

6.8 OXIDATION

6.8.1 OXIDATION OF POLYBUTADIENE USING $PdCl_2/CuCl_2.2H_2O$ WITH WATER[109]

In a 45 cm^3 autoclave equipped with a glass liner containing a stirring bar and DME (6 cm^3) was placed palladium chloride (0.046 g, 0.26 mmol) and copper chloride dihydrate (0.85 g, 5 mmol). To this mixture was added a DME (4 cm^3) solution of polybutadiene (0.27 g; 5mmol) followed by the addition of water (5 cm^3). The autoclave was purged with oxygen, pressurised to 300 psi and heated to 80°C for 24 hours. The autoclave was then cooled to room temperature, oxygen was vented and re-dissolved in DME, the polymer product was extracted with ethyl acetate and the organic layer was dried with $MgSO_4$ and evaporated to give the polymer product which was analysed by NMR in DMSO-d_6.

6.8.2 CATALYTIC OXIDATION OF POLYBUTADIENE USING $RhCl_3.3H_2O$-$Cu(ClO_4)_2(HMPA)_4$[101]

Catalyst components rhodium trichloride (0.0262 g; 0.1 mmol) and copper perchlorate (0.0542 g, 0.2 mmol) were dissolved in ethanol (10 cm^3) and left to equilibrate for 15 minutes. Oxygen was bubbled through the catalyst solution and to this was added a polybutadiene (3.1420 g; 58 mmol) solution in ethanol (12 cm^3) and dichloromethane (120 cm^3) followed by water (9cm^3; 50 mmol). The mixture was left to react for 4 hours. Analysis of the product by NMR indicated that no reaction had occurred as only the starting material was observed.

6.8.3 HYDROBORATION-OXIDATION OF POLYBUTADIENE[69,110]

A 9-BBN THF solution (150 cm^3) was added under nitrogen to a round bottomed Schlenk flask containing a cooled (-10°C) solution of polybutadiene (2.7 g; 50 mmol) in THF (150 cm^3) and left to stir at this temperature for 1-2 hours. The reaction mixture was then cooled further (25°C) and degassed sodium hydroxide (10 cm^3, 6M) was added via a catheter to the reaction flask. Hydrogen peroxide (20 cm^3, 30 %) was then added dropwise via a catheter. The resultant mixture was left at this temperature for 1 hour and then allowed to warm (40°C) to ensure complete reaction. The polymer product was then precipitated using water and re-dissolved in methanol to extract any boric acid via distillation. The product was then re precipitated using water and dissolved in d_4-methanol for analysis by nmr.

SECONDARY ALCOHOL TO A KETONE

6.8.4 OXIDATION OF POLYBUTADIENE ALCOHOL WITH $VO(acac)_2$-Bu^tOOH COMPLEX[102]

To a methanol (65 cm^3) solution of the polybutadiene alcohol (0.72 g; 10 mmol) Bu^tOOH (1.0 g; 11.11 mmol) in 2,2,4-trimethyl pentane (8 cm^3) was added and stirred the mixture for 5 minutes. The polybutadiene alcohol-Bu^tOOH solution was then added to a preweighed amount of $VO(acac)_2$ (green) (0.28g; 1.1 mmol) under nitrogen., the solution immediately turned red/brown in colour. The solution was then allowed to reflux for 15 minutes after which time the polymer had fallen out of solution, the remain solution was therefore cathetered off into another Schlenk flask leaving the solid polymer behind which readily dissolved in methanol indicating the reaction had not been successful, this was later confirmed by nmr.

6.8.5 OXIDATION OF POLYBUTADIENE ALCOHOL WITH ACTIVATED DMSO WITH OXALYL CHLORIDE[103]

Oxalyl chloride (1.16 g; 11 mmol) was added to a 2-neck schlenk equipped with a stirrer and a thermometer. The oxalyl chloride was cooled to -60°C and the DMSO (1.46 g; 24 mmol) was added dropwise while continually stirring over 5 minutes. The DMSO (30 cm^3) polybutadiene alcohol (0.72 g; 10 mmol) solution was added dropwise to the DMSO/oxalyl chloride at -60°C over 5 minutes. The reaction mixture was stirred for 15 minutes and triethylamine was added in over 5 minutes at -60°C. The cooling bath was removed allowing the reaction solution to reach room temperature. The DMSO solution was removed from the solid products formed, these were washed several times with water and then analysed by FTIR and nmr.

6.8.6 OXIDATION OF POLYBUTADIENE ALCOHOL WITH 4-METHOXY-2,2,6,6-TETRAMETHYLPIPERIDINIUM CHLORIDE[104,105]

Part A: Preparation of 4-methoxy-2,2,6,6-tetramethylpiperidiniumchloride

Step 1: Preparation of 4-methoxy-2,2,6,6-tetramethylpiperidinyl-1-oxy

To a stirred solution of 4-hydroxy-2,2,6,6-tetramethyl piperdinium-1-oxy (II) (17.2g; 100 mmol) in anhydrous DMF (150 cm^3) was added NaH (3.6g; 150 mmol). After this suspension was stirred under nitrogen, methyl iodide (9.34 cm^3; 150 mmol) was dissolved in DMF (34 cm^3) and added dropwise to the solution at 0°C, the reaction mixture then stood at room temperature for 5 hour. After filtration of NaI, ether (500cm^3) was added. The resulting mixture was washed and separated, and the ether layer was dried with anhydrous magnesium sulphate. The ether solution was concentrated in vac to give a viscous red liquid. n-Hexane was added and the compound was crystallised at -20°C. (14.5g, 77.9 mmol, 78% yield).

Step 2: 4-methoxy-2,2,6,6-tetramethylpiperidinium chloride

Anhydrous chlorine was bubbled into the stirred solution of 4-methoxy-2,2,6,6-tetramethylpiperidinyl -1-oxy (2.0g; 10.7 mmol) in CCl_4 (100 cm^3). The orange precipitate was filtered and washed with CCl_4 to give a product thought to be 4-methoxy-2,2,6,6-tetramethylpiperidinium chloride (1.98 g; 9.5 mmol, 83% yield), mpt 129-131°C decomposition

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Part B: Oxidation of polybutadiene alcohol

A solution of the 4-methoxy-2,2,6,6-tetramethylpiperidinium chloride (0.22 g; 1 mmol) was prepared in CH_2Cl_2 (20cm^3), this was added to a stirred suspension of the polybutadiene alcohol (3.6 g; 50 mmol) in CH_2Cl_2 (80 cm^3) under nitrogen in the absence of light.

6.8.7 SELECTIVE OXIDATION OF ALCOHOLS WITH TRICHLOROMELAMINE[107]

Trichloromelamine (2.25 g; 10 mmol) was added to a solution of polybutadiene diol (0.54 g; 10 mmol) or polyvinylalcohol (0.44 g; 10 mmol) in dichloromethane (50 cm^3). The reaction mixture was stirred vigorously at room temperature for three hours. The solid was filtered and the organic layer was analysed by NMR and IR as unchanged starting material.

6.8.8 *cis*-DIHYDROXYLATION OF POLYBUTADIENE

6.8.8.1 DIHYDROXYLATION OF POLYBUTADIENE USING AD-MIX[112]

1 Model reaction in t-BuOH/water solvent system

A round bottom flask (50 cm^3) was charged with tert-butanol (5 cm^3), water (5 cm^3) and AD-mix (1.4 g). Methane sulphonamide was then added (95 mg, 1equiv - based on 1 mmol of alkene). The mixture was stirred at room temperature until both phases were clear. The *cis*-3-hexene (1 mmol) was added to the 2 phase reaction mixture and stirred vigorously for 24 hours. The reaction was quenched with sodium sulphite (1.5 g), stirred for 60 minutes and extracted several times using dichloromethane. The combine dichloromethane layers were washed with KOH (2N) to remove most of the sulphonamide, dried ($MgSO_4$) and concentrated to give a mixture containing the product.

2. Reactions involving polybutadiene

A round bottom flask (100 cm^3) was charged with a solution of polybutadiene (1mmol) in THF or CH_2Cl_2 (20 cm^3), to this was added AD-mix (1.4 g) in water (20 cm^3). Methane sulphonamide was added (95 mg, 1equiv - based on 1 mmol of alkene) and the mixture was stirred vigorously at room temperature for 24 hours. The reaction was quenched with sodium sulphite (1.5 g), stirred for 60 minutes and extracted several times using dichloromethane. The combine dichloromethane layers were washed with KOH (2 $moldm^{-3}$) to remove most of the sulphonamide, dried ($MgSO_4$) and concentrated to give a mixture containing the product, which was indicated by NMR to be unreacted polybutadiene.

3. Polymer reactions with phase transfer agent. (trimethyl ammonium bromide)

A round bottom flask (100 cm^3) was charged with a solution of polybutadiene (0.05 g; 1 mmol) in THF or CH_2Cl_2 (20 cm^3), to this was added AD-mix (1.4 g) in water (20 cm^3). Methane sulphonamide (0.095 g, 1equiv - based on 1 mmol of alkene) and trimethyl ammonium bromide (0.5 g) were added and the mixture stirred vigorously at room temperature for 24 hours. The reaction was quenched with sodium sulphite (1.5 g), stirred for 60 minutes and extracted several times using dichloromethane. The combined dichloromethane layers were washed with KOH (2N) to remove most of the sulphonamide, dried ($MgSO_4$) and concentrated but no polymer was observed, indicating the polymer was water soluble and resided in the aqueous layer.

6.8.8.2 DIHYDROXYLATION OF POLYBUTADIENE USING PERMANGANATE ION

1 Polymer reaction without phase transfer agent

A solution of potassium permanganate (2.34 g, 14.8 mmol) and sodium hydroxide (0.5 g, 12.5 mmol) in water (80 cm^3), cooled to 0°C, was added quickly with vigorous stirring to a cold mixture of dichloromethane (100 cm^3), water (20 cm^3) and cracked ice (50 g) containing polybutadiene (0.54 g, 10 mmol). After 24 hours the solution was removed via a filter-stick and catheter from the manganese dioxide precipitate. The dichloromethane was then removed under vacuum to give the unreacted polymer.

2 Polymer reaction with phase transfer agent

A solution of potassium permanganate (2.34 g, 14.8 mmol) and sodium hydroxide (0.5 g, 12.5 mmol) in water (80 cm^3), cooled to 0°C, was added quickly with vigorous stirring to a cold mixture of dichloromethane (100 cm^3), water (20 cm^3) and cracked ice containing (50 g) containing polybutadiene (0.54 g, 10 mmol) and trimethyl ammonium bromide (0.5 g). After 24 hours the solution was removed via a filter-stick and catheter from the manganese dioxide precipitate. The dichloromethane was then removed under vacuum, however, no polymer was found. The polymer may be water soluble and therefore still within the water/magnesium dioxide layer.

6.8.9 *trans*-DIHYROXYLATION OF POLYBUTADIENE

Epoxidised polybutadiene was dissolved in CH_2Cl_2 (50 cm^3) and treated with MoO_2Cl_2L (0.5g) in CH_2Cl_2 (10 cm^3) and water (0.5 cm^3). The solution was refluxed for 24 hrs. NMR analysis of the product indicated that diol had been formed but had not significantly reduced the epoxide.

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